明　細　書

1. 発明の名称
　超伝導体、超伝導製品及び製法
2. 特許請求の範囲
　1. 結晶基板上に、タリウム、任意成分として
のカルシウム、バリウム及び銅の酸化物からなり、
厚さが少なくとも30Aでc軸が結晶基板表面に
垂直に配向している配向超伝導層を包含する超伝
導物品。
　2. 前記超伝導層が、前記基板にエピタキシャ
ル成長したものである特許請求の範囲第1項に記
載の超伝導物品。
　3. 前記超伝導層が2122組成を有している特許
請求の範囲第1項に記載の超伝導物品。
　4. 前記超伝導層が2223組成を有している特許
請求の範囲第1項に記載の超伝導物品。
　5. 前記基板が酸化マグネシウム又はイットリ
ア安定化ジルコニアである特許請求の範囲第1項
に記載の超伝導物品。
　6. 酸化マグネシウム上に、タリウム、バリウ

ム、カルシウム及び銅の酸化物の超伝導エピタキ
シャル層を包含する超伝導物品。
　7. 前記層が配向している特許請求の範囲第6
項に記載の超伝導物品。
　8. 前記超伝導層が2122組成である特許請求の
範囲第7項に記載の超伝導物品。
　9. 前記超伝導層の厚さが約1μmである特許
請求の範囲第1項、第6項及び第8項のいずれか
に記載の物品を包含するマイクロ波又はミリメー
ター装置。
　10. アンテナからのシグナル受信関係における
ダイオード；
　パワースプリッタ；
　位相検出器；
　結晶基板上に、タリウム、任意成分としてのカ
ルシウム、バリウム及び銅の酸化物からなり、厚
さが少なくとも30Aでc軸が結晶基板表面に垂
直に配向しており且つ長いワイヤの形態をしてい
る配向超伝導層を包含する遅延線路；
　前記ダイオードを前記パワースプリッタ及び前

（1）

（2）

記パワースプリッタを前記位相検出器に接続している手段；並びに

前記位相検出器を出力に接続するための手段を包含するデジタル瞬時周波数測定装置。

11. 結晶基板上に、タリウム、任意成分としてのカルシウム、バリウム及び銅の酸化物からなり、厚さが少なくとも30Aでc軸が結晶基板表面に垂直に配向しており且つ前記基板上に塗布した段付きストリップの形態をしている配向超伝導層を包含する、アンテナから信号を受信するためのマイクロ波フィルター；

ミクサ；

掃引局部発振器；

分散性遅延線路；

前記マイクロ波フィルター及び掃引局部発振器を前記ミクサ並びに前記ミクサを前記分散性遅延線路に接続するための手段；並びに

前記分散性遅延線路を出力に接続するための手段を包含するマイクロ波受信器。

12. タリウム、任意成分としてのカルシウム、

バリウム及び銅の酸化物からなり、厚さが少なくとも30Aでc軸が結晶基板表面に垂直に配向している配向超伝導層を包含する超伝導物品の製造方法において、

結晶基板表面を、高温において、タリウム、カルシウム、バリウム及び銅の酸化物を含有する液相で塗布し、

前記溶液を冷却することにより、前記金属酸化物が表面で結晶化して、前記基板上に酸化物の形態で、前記金属酸化物の超伝導層を形成することを包含する超伝導物品の製造方法。

13. タリウム、任意成分としてのカルシウム、バリウム及び銅の酸化物からなり、厚さが少なくとも30Aでc軸が結晶基板表面に垂直に配向している配向超伝導層を包含する超伝導物品の製造方法において、

結晶基板表面を、タリウム、カルシウム、バリウム及び銅カルボキシレート石鹸の溶液で塗布して塗膜を生成し、

酸素の存在下及び所定の割合の前記酸化物のう

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(3)

ちの少なくとも酸化タリウムの超過圧力の存在下で、前記石鹸塗膜を高温で、前記基板上に酸化物の形態の前記金属の超伝導層が生成するのに十分な時間熱分解することを包含する超伝導物品の製造方法。

14. 前記超過圧力が、少なくともタリウム及びカルシウムオキシドのペレットを前記塗膜から機械的に除去することによって供給される特許請求の範囲第13項に記載の方法。

15. 前記石鹸を、前記熱分解よりも低い温度で前記石鹸を予備熱分解する更なる工程を包含する特許請求の範囲第13項に記載の方法。

16. 前記予備熱分解を250 〜450 ℃の温度で行い、前記熱分解を700 〜950 ℃の温度で行う特許請求の範囲第15項に記載の方法。

17. 前記石鹸が2 −エチルヘキソエートである特許請求の範囲第13項に記載の方法。

18. 前記石鹸がネオデカノエートである特許請求の範囲第17項に記載の方法。

19. 前記基板が酸化マグネシウム又はイットリ

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ア安定化ジルコニアである特許請求の範囲第13項に記載の方法。

20. 酸化雰囲気中でのレーザアブレーションを用いた、タリウム、バリウム、カルシウム及び銅の酸化物から実質的になる超伝導フィルムを形成する方法において、

タリウム、任意成分としてのカルシウム、バリウム及び銅の酸化物を包含するターゲットを、ターゲットの存在下で酸素源を包含するタリウム及び酸化雰囲気においてレーザアブレーションを行うことにより、プルーム状の原子が生成して前記ターゲットの方向に向い、前記原子が前記ターゲット表面に衝突して結合し、

高温超伝導組成物を生成する条件下でアニーリングを行い、

前記原子を前記ターゲット表面で冷却して超伝導酸化物層を生成する、以上の工程を包含する超伝導フィルムを形成する方法。

21. アブレーションに使用したレーザ以外のエネルギー源で前記酸素源を活性化する特許請求の

範囲第20項に記載の方法。

22. 前記酸素源が、過酸化水素、オゾン又は酸化窒素である特許請求の範囲第20項に記載の方法。

23. タリウム、任意成分としてのカルシウム、バリウム及び銅の酸化物からなり、厚さが少なくとも30Aでc軸が結晶基板表面に垂直に配向している配向超伝導層を包含する超伝導物品の製造方法において、

タリウム、任意成分としてのカルシウム、バリウム及び銅の酸化物の混合物を高温に加熱して結晶性超伝導層の生成に適当な組成を有する液体を生成し、

前記高温で前記結晶基板を前記液体に浸漬し、

前記液体を約10〜50℃で冷却するか又は前記液体の一部分を蒸発して超伝導体の結晶化を誘発し、前記液体の本体を除去して前記基板上に層を残存させる、以上の工程を包含する超伝導物品の製造方法。

24. タリウム、カルシウム、バリウム及び銅の酸化物からなり、厚さが少なくとも30Aでc軸

が結晶基板表面に垂直に配向している配向超伝導層を包含する超伝導物品の製造方法において、

前記基板に、タリウム及びカルシウムの酸化物からなる第一被膜を塗布し、

前記第一被膜に、原子比が超伝導層の生成に適当であるバリウム及び銅の酸化物を包含する第二被膜を塗布し、

前記被膜を液化温度に加熱することにより、前記タリウム及びカルシウムの酸化物が液体となって前記バリウム及び銅の酸化物を溶解し、

前記液体を冷却して超伝導層を生成する、以上の工程を包含する超伝導物品の製造方法。

25. 前記第二被膜がタリウム及びカルシウムの酸化物を包含している特許請求の範囲第24項に記載の方法。

26. 前記第一被膜を、カルボン酸タリウム及びカルボン酸カルシウムを熱分解して、それらの酸化物を生成することにより生成する特許請求の範囲第24項に記載の方法。

3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は、タリウムを主成分とする超伝導体の製造方法、得られる組成物及びこのような組成物を用いた装置に関する。

〔従来の技術及び発明が解決しようとする課題〕

高温超伝導における最近の科学的変化は、超伝導転移温度(T_c) が著しく高い数多くの新規な金属酸化物化合物、特に銅酸化物化合物の発見から生じた。最初に発見された化合物は、ほとんどの場合、銅と結合したバリウム及びイットリウム等のアルカリ土類金属と希土類金属との組み合わせを主成分とするものであった。より最近では、組成物が種々の化学量論量でタリウム、カルシウム、バリウム、銅及び酸素を有する、タリウムを主成分とする超伝導体が製造された。タリウムCa−Ba−Cu−O 付着層は処理温度で液体である組成とすることができるので、タリウム材料は処理することが困難であった。タリウム酸化物は処理温度の

約500 ℃で比較的高い蒸気圧を有するため、結晶構造が適切な化学量論量を確実に有するように処理するのが増々困難となった。ほとんどの場合、密封したAu又はPtアンプルを用いて、高温処理中にフィルム上にTlの制御された超過圧力及び酸素を発生させることにより、Tlの揮発を制御している。

超伝導フィルムには非常に重要な面がある。しかしながら、有用であるためには、フィルムは、十分に均一でなければならず、装置の電流条件を満足することができ、好ましくは液体窒素の温度よりもかなり高い超伝導転移温度を有し、銅よりもはるかに低いRF表面抵抗を有し且つ再現性よく製造できなければならない。

サンディア ナショナル ラボラトリーズ(Sandia National Laboratories)のギンレー(Ginley)等は、2122タリウム化合物(Tl_2、Ca、Ba_2、Cu_2、O_8) の超伝導薄膜の製造について報告を行った。又、同じ研究所のジム クワク(Jim Kwak)は、イットリア安定化ジルコニア上に設けた多結晶タリ

ウムを主成分とするフィルムについての報告を行った。上記のフィルムは、基板上に個々の金属を順次電子ビーム蒸着後、密閉白金るつぼ中で後蒸着反応工程を行うことにより、イットリア安定化ジルコニア上に形成されていた。得られたフィルムは、無配向であり、転移温度は97 °K であった。アイビーエム社(IBM) は、無線周波数(rf)ダイオードスパッタリングによる2223及び2122化合物の配向薄膜の製造についての報告を行った。

一方、タリウム化合物に関して、多数の論文が発表されている。これらの論文の代表的なものとしては下記のものが挙げられる：シェング(Sheng)及びハーマン(Hermann) 、ネーチャー(Nature)、第332 巻、55〜58(1988) ；シェング(Sheng) 及びハーマン(Hermann) 、ネーチャー(Nature)、第332 巻、138 〜139(1988) ；ギンレー(Ginley)等、フィズィカC、第152 巻、217 〜222(1988) ；スーパーコンダクター　ウイーク(Superconductor Week) 、第2 巻、第18号、1988年5 月9 日発行では、サンディア(Sandia)が、77 °K での臨界電流

密度が110,000 A/cm² に達し、Tc が97 °K である無配向多結晶性TL薄膜を製造したことを報告している。高磁場(6テスラ) の存在下で観察された臨界電流密度は、4 °K で1 x 10⁶ A/cm² であった。

ベンカテサン(Venkatesan)等、アプル　フィズ　レター(Appl. Phys. Lett.) 、第52巻、1193〜1195(1988) 及びウー(Wu)等、プロシーディングズ　オブ　エスピーアイイー　シンポジウム　オン　ハイ　Tc スーパーコンダクターズ(Proceedings of SPIE symposium on High Tc Superconuductors) 、カリホルニア州のニューポートビーチ、1988年3 月では、高Tc 超伝導薄膜の製造にパルスレーザ蒸着を用いることが報告されている。上記したベンカテサン(Venkatesan)等及びウー(Wu)等では、650 ℃で蒸着後に450 ℃でアニールすることにより超伝導を示すYBaCuOフィルムを得たとしている。ウイタナッチ(Witanachchi) 等〔刊行物であるアプル　フィズ　レター(Appl. Phys. Lett.) 〕は、高Tc 超伝導YBaCuO薄膜のレーザ

(11)　　　　　　　　　　　(12)

アブレーション中に直流バイアスプラズマを加えることにより、400 ℃の低い基板温度で、そのまま超伝導フィルムが得られるとの報告をしている。

〔課題を解決するための手段及び作用〕

液相から結晶基板上に成長させるプロセスを用いることにより、タリウムを主成分とする超伝導フィルムが基板上で提供される。又、基板上に超伝導性物質の結晶性層を生成し、ある場合にはエビタキシャル成長を行うための種々の手法及び条件が提供される。生成物は、表面インピーダンスから分かるように優れた超伝導特性を有するとともに、マイクロ波及びミリメータ波の用途に用いられる電子装置の部品として独特な用途がある。

本発明により、薄膜状のタリウムを主成分とする超伝導体組成物の製造方法、得られる組成物及び装置に関する。組成物は、種々の基板、特に結晶性基板上に、平均組成Tl.Ca_{n−1} 、Ba₂Cu_nO_{2n+4} をフィルムの形態で包含している。これらのフィ

ルムを製造するのに用いられる方法は、化学付着法及び物理付着法の両方であり、好ましいものとしては、ゾルーゲル法及びレーザアブレーション法が挙げられる。超伝導体層塗工基板は、多種多様の電子装置、特にマイクロ波及びミリメータ波用途における部品として使用される。

提供されるフィルムは、2021、2122、2223を含めた化学量論量又は用いることのできる他の化学量論量を有する主にタリウムー(カルシウム) ーバリウムー銅酸化物である。これらのフィルムは、実質的に均一な結晶化度を有するように配向させたフィルムである。又、これらのフィルムは、単結晶から構成されていても、又は結晶粒界で結合している複数の結晶から構成されていてもよい。これらのフィルムが、高度に配向していて、c 軸が基板表面に垂直であることは、X 線解析又は電子ビームチャネリング法によって確認できる。必要に応じて、相又は関連相の2 つ混合物をフィルム内に生成することができるが、ほとんどの場合、単相フィルムが得られる。用途によっては、多結

(13)　　　　　　　　　　　(14)

晶性フィルムも製造できる。

　フィルムの厚さは制御できる。即ち、フィルムは、個々の用途に応じて、1層で超伝導を得るのに必要な面の全てを含んでいる場合には1層の厚さ（一般的に約30～50Å）でよく、又は、2μm以上の厚いものであってもよい。フィルムの厚さは、用いられる操作で大きく限定されるのではなく、主に実用的な観点から決まる。

　多くの用途の場合、1μmの何分の1かの厚さ、一般的に約0.1～1μmの範囲で用いられる。今までの超伝導転移温度は実質的に約150°K未満であったのに対して、このフィルムの超伝導転移温度は、少なくとも75°K、より一般的には90°K、好ましくは少なくとも約100°K、より好ましくは約115°K、特に好ましくは少なくとも約122°Kである。T_cが少なくとも110°Kである2122組成フィルム及びT_cが少なくとも122°Kである2223組成フィルムを得ることができる。場合によっては、一つのパラメータを別のパラメータのために譲歩することはあるが、超伝導転移

温度はできるだけ高くなければならない。ほとんどの場合、フィルムは、約60～100°Kの温度で使用される。

　フィルムの臨界電流密度は、通常、77°Kで少なくとも10^3A/cm^{2}であり、より一般的には約10^6A/cm^{2}である。マイクロ波及びミリメートル波の用途の場合、表面抵抗又はインピーダンスは、一般的に、10GHz及び50°Kを超える温度、好ましくは約75°Kを超える温度で、約10^{-3}Ω未満、より一般的には約10^{-4}Ω未満である。

　フィルムは、実質的に異物を含んでおらず、超伝導結晶と関係のない物質の含有量は、約10重量%未満、好ましくは約5重量%である。ほとんどの場合、フィルムの最小寸法は少なくとも約0.5cmであり、a、b面における最小寸法は3cm又は5cm以上もある。

　これらのフィルムは、格子欠陥密度が低く、高品質であることが分かる。「格子欠陥密度が低い」とは、真性超伝導物理的輸送特性を示し且つ必要とする装置特性要件を十分に達成するのに十分な

程度に低い欠陥密度を意味する。更に、表面形を平滑にするだけでなく、厚みを均一にすることができる。Nb$_3$Sn超伝導体の表面形態及び電磁特性への影響については、ホルシス(Forsyth)、サイエンス(Science)、第242巻、391～399(1988)を参照できる。

　更に、超伝導体の結晶格子と基板の結晶格子との差が10%を超えない場合には、フィルムを基板上にエピタキシャル成長してもよい。即ち、結晶のa軸に沿って、a軸間の格子パラメータの差〔(a基板－a超伝導体)/a基板〕は、最大約10%まであってもよく、この場合には、エピタキシャル成長が可能である。エピタキシーが望ましいが、高度に配向したc軸垂直フィルムを得る必要はない。しかしながら、目的とするフィルムの場合、高度に配向することの他に、基板を適当に選択することによって、エピタキシーも達成することができる。

　軸上の公称配向度から数度の固有ずれを有するMgOの（100）表面上にエピタキシャルTl 2223

及び2122フィルムを設けるのが有益である。Tl 2223フィルムの場合、<001>軸（格子パラメータ、c＝36.26Å）は、MgO基板の<001>軸と一致するか、又はエピタキシーにおいて系統的な角度のずれがあるとともに格子の不一致が大きい。<001>軸の相関関係の他に、エピタキシャルTlフィルムでは、<100>軸及び<010>軸がMgO基板の類似軸と平行であるか又は体系的にずれがある。

　塗工基板の個々の用途、エピタキシーを所望かどうか、個々の処理条件等に応じて、単結晶、多結晶及び非晶質基板を含む種々の基板を用いることができる。基板として用いることのできるものとしては、酸化マグネシウム、イットリア安定化ジルコニア、サファイア、アルミナ、シリコン、アルミン酸ランタン、チタン酸ストロンチウム、ヒ化ガリウム、ガリウム酸ランタン及びフッ化カシウムが挙げられる。

　又、固形基板上にタリウムを主成分とする超伝導体を製造するには種々の手法が用いられる。他の超伝導体金属酸化物組成物の場合に今まで用い

られてきた手法としては、レーザーアブレーショ
ン、サーマルエバポレーション、液相エピタキシ
ー、電子ビーム、マグネトロンスパッタリング及
び化学蒸着等が挙げられる。目的とするエピタキ
シャル層を製造するための方法の代表例としては、
ゾルーゲル被膜及びレーザアブレーション付着被
膜の液相熱処理が挙げられる。

　液相フィルム生成では、付着フィルムを加熱し
て基板上に液体被膜を形成することにより、金属
酸化物を基板上に液体から結晶化させて超伝導層
を形成する。Tl酸化物自体又は溶媒としての酸化
カルシウムと組み合わせ、他の酸化物を高温でTl
酸化物含有液体に溶解させて液体組成物を生成後、
適切な化学量論量で結晶化することができる。冷
却、溶媒の蒸発又は化学沈殿を行うと、金属酸化
物が結晶化して結晶性超伝導体層が生成する。基
板によっては、この層はエピタキシャル層であっ
もよい。対イオン及び条件により所望の酸化物が
生じる場合には、最初から酸化物を使用する必要
はなく、液相における金属源として役立つ金属化

合物を用いることができる。このプロセスは、下
記の構成要素に分けることができる：（1）基板
の被覆；（2）結晶化中の環境；及び（3）温度、圧
力、時間等のサーマルプロセス条件；（4）他の種
々の事柄。

　エピタキシャル成長の場合、一定の結果を得る
ためには、基板を予備処理する必要がある。液相
エピタキシャル操作には、高度に研磨された表面
を有する基板を用いる。この表面は、機械的又は
化学的、好ましくは両方の手段で研磨される。単
結晶基板を用いると、エピタキシャルフィルム構
造が得られる。例えば、酸化マグネシウム<100>
を、熱濃縮リン酸を用いて、例えば、85％リン酸
を用いて約80℃で10分間研磨するか、又は表面を
平らに且つ所望の配向となるまで磨いた後50℃の
濃リン酸に1〜3分間浸漬することにより研磨す
ることができる。得られる化学研磨した結晶表面
は非常に清浄で且つ実質的に欠陥のない表面であ
る。表面を研磨する具体的方法は、本発明におい
ては重要ではない。酸化マグネシウムの代表例と

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しては、（100）面表面を用いるのが好ましい。

　基板の被覆は種々の方法で行うことができる。
一手法としては、熱分解により被膜として所望の
酸化物を生成することができる化学前駆体を用い
ることが挙げられる。別の手法として、超伝導体
の製造に適当な化学量論量を有する金属酸化物を
用いることが挙げられる。更に、気相蒸着を包含
する他の手法を用いてもよい。考慮すべき最初の
手法では、酸化物を生成するために有機金属前駆
体を用いる。

　ゾル組成物は、適当な化学量論量を有する金属
石鹸を用いて調製することができる。石鹸は、炭
素数が少なくとも約6個、好ましくは少なくとも
約8個、一般的に16個以上、より一般的に12個以
上のカルボン酸塩である。2−エチルーヘキサノ
エートが好ましく用いられるが、ネオデカノエー
ト又は他の分岐鎖、特にα分岐鎖脂肪酸化物も用
いることができる。金属石鹸は、従来の方法を用
いて製造することができる。これらの石鹸は、適
当な媒体、特に、クロロホルム、トルエン、キシ

レン、ベンゼン、メチレンジクロリド等の沸点が
約40℃〜100℃の炭化水素又はハロ炭化水素
に分散し、混合物を数時間撹拌、例えば、振盪し
て均一にする。増粘剤、例えば、多糖類又は超高
分子量ポリマー等の補助剤を添加してもよい。そ
の後、得られる溶液及び/又は分散液を基板に塗
布する。

　塗布は、粘稠なゾルを塗布すべき表面に置き、
その表面を遠心分離により短時間回転して、フィ
ルムを実質的に均一に分布させる。又、塗布すべ
きでない部分を保護して、基板を分散液に浸漬す
るか又は分散液で噴霧してもよい。基板上にフィ
ルムが実質的に均一に塗布されるいずれの手法を
用いてもよい。

　次に、塗工基板を、一般的に約150℃〜500℃
の範囲、好ましくは約150℃〜300℃の範囲の高
温で短時間熱分解する。100℃の低温でTlの揮発
が生じる結果、プロセスタイミングを短く且つTl
超過圧力及び酸化雰囲気を用いて、相生成を制御
し且つTl損失及びフィルム中の望ましくない第二

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相の生成を抑制する。熱分解時間及び温度は、脂肪酸が確実に分解して金属酸化物の薄膜が残存するように選択する必要がある。熱分解は、酸素の、好ましくは空気の存在下で生じさせる。この操作は、必要なだけ何回も繰り返して、金属酸化物フィルムの厚さを増加させる。

順次行われる各熱分解は、最初の熱分解よりも低い温度で行うことができる。この場合、最初の熱分解を温度範囲の上限部分、即ち、250～450℃で行い、その後の熱分解を約200～350℃の範囲の温度で行う。通常、少なくとも約60％の揮発性有機物質を除去し、加熱時間を延長することにより、一定重量となる。300℃を超える温度で熱分解を行う場合には、タリウムの揮発をできるだけ少なく抑えるように注意しなければならない。

フィルムの付着及び熱分解操作は、少なくとも1回、より一般的には2回行われ、5回以上行うことができ、通常の回数は約4回以下である。

各の層の厚さは、下記の多数のパラメータによって異なる：ゾルの粘度、回転時間、回転数、基

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基板の大きさの約0.001～10倍の容積を意味する。更に、超伝導体層の表面と比較して、タリウム源の表面は比較的大きくなければならず、少なくとも約1.5倍、好ましくは約2倍、場合によっては5倍以上である。更に、酸化タリウムは、酸化カルシウム及び酸化銅と組み合わせるのが好ましく、この場合、結晶成長にソースが存在するかどうかによって、又は適切な相となった後にタリウム超伝導体材料を安定化するために、組成を変化させてもよい。

気相では、加熱中に、空気、純酸素又は他の酸化性酸素源、例えば、過酸化水素又はオゾンを用いるのがよい。ペレットの組成は、製造したい個々のタリウム超伝導体によって異なる。例えば、2223組成の場合、ペレットのTl：Ca：Ba：Cuモル比は1：3：1：3である。不活性管は、好ましくは不動態化貴金属、最も好ましくは金又はめっきした石英である。この管は、反応中の圧力に耐えるために外部から補強してもよい。

処理温度は、少なくとも約600℃、より一般

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板を回転する温度等。浸漬、噴霧、ブレードを用いた塗布等の他の手法を用いて被膜を生成する場合には、異なるパラメータが関与する場合がある。

基板表面を所望の程度に塗布した後、基板は、加熱中に酸素源の存在下で化学量論量を維持するのに適当なモル比を有するペレットが入っている密閉した不活性容器中に導入することができる。ペレットのモル比は、フィルム内において望まれる相により決まる。加熱後のフィルム組成は、ソース物質の形状及び温度並びに得られるTi超過圧力の影響を受ける。

制御タリウム超過圧力の維持は、種々の方法で行うことができる。最も簡単な方法は、酸化物混合物を含有している層に酸化タリウムを塗布し、酸化タリウムオーバーコートを蒸発させてタリウム超過圧力を提供することである。十分なタリウムを超伝導体層に確実に組み入れるためには、超伝導体層の熱処理用のハウジングは比較的小さいのが好ましく、この場合、蒸気が占有するのは比較的小さい容積である。「比較的小さい」とは、

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には約630℃で且つ約950℃以下、しばしば約800～900℃である。温度は、適当な方法（熱電対が都合がよい）で監視できる。通常、処理温度には迅速に達し、一般的には5分以内、好ましくは3分以内、より一般的には約0.5～3分で達する。もっと加熱速度を小さくして（20℃/分）、粒子サイズがもっと小さい超伝導フィルムを連続的に生じさせてもよい。管は、上記した範囲の温度で、一般的に、残留炭素化合物を確実に完全に熱分解し且つ原子が適当な格子構造をとるのに十分な時間加熱できる。一般的に、高温での加熱時間は、少なくとも約0.5分で且つ約60分以下であり、より一般的には、約0.5～25分、好ましくは約0.5～10分である。この時間の終わりに、管を加熱源から取り出して冷却できる。通常、急冷には何の努力を必要とせず、温度を急激に減少させるようにしなくても、管を室温環境におけばよい。目的とするフィルムを製造するための第二の好ましい方法は、レーザーアブレーションを用いるものである。レーザーアブレーションは、上記したサー

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マルプロセスの準備において室温で基板の塗布を行うのに用いるか、又は超伝導相を高温で一工程で付着及び生成するのに用いることができる。

　本発明によれば、レーザーアブレーションは適当なターゲットを準備して行う。ほとんどの場合、装置は従来のものであり、上記したウー(Wu)等に記載されている。ターゲットは、金属又は金属酸化物の適当な組成物を、制御された速度で回転できる支持体の表面に配置することにより準備する。支持体上に配置したターゲットを、石英窓を有する真空チャンバーに入れ、適当なエネルギー及び波長を有するレーザービームをターゲットに当てて、ターゲット表面に対して垂直な融除蒸気のプルームを生じさせる。基板をプルームの方向に対して垂直に配置してプルーム中の原子を受け取るようにする。このことにより、原子が基板表面に結合する。目的とする付着物が非晶質であるか又は結晶質であるかによって、基板を、室温又は高温に維持する。

　レーザーアブレーションターゲットは、上記し

たゾルーゲルコーティングと同様の方法で作製することができる。このようにして、種々のカルボン酸塩の均一なフィルムを製造し、上記したようにして熱分解して所望の酸化物混合物を生成することができる。熱分解は、酸素の存在下で行い、適当な酸化状態における所望の金属酸化物を確実に生成することができる。又、ターゲットは、圧縮且つ燒結した粉末又は熱間圧縮した粉末から作製することもできる。

　ターゲット上でのレーザーエネルギー密度は、一般的に約1～3J/cm²である。ターゲット上のフィルムは、基板上の意図する組成物と同じ金属モル比を有する。ターゲットは、通常、表面積が約0.5～10平方インチであり、厚さが約0.001～0.25インチである。

　レーザーを集束して、ターゲットの種々の部分を処理することができる。このレーザーは、最小約2°～最大90°の広範囲の角度にわたって表面に当てることができる。一般的な衝突角度は約25°である。レーザーが当たる面積は、一般的に、

少なくとも約2mm²で且つ約50mm²以下である。一般的な面積は、約15mm²である。幅に対する長さの比は、衝突角度によって異なり、一般的に少なくとも2：1で且つ約20：1以下であり、より一般的には約10：1である。パルス当たり約2J/cm²の範囲のエネルギーを用いることにより、各パルスで、基板上に、一般的に約3Aの厚さを有する一つの単分子層を付着させることができる。1秒当たりのパルス数を制御（一般的に約0.5～50の範囲）することにより、基板上に約0.1μm／分で増加させることができる。

　ターゲットは、通常、基板に比較的近接しており、通常約2cm以上で且つ約10cm以下、好ましくは約6cm以下である。チャンバーを、約500mTorr、好ましくは約2～200mTorr、より好ましくは約100～200mTorrになるまで排気する。酸素、空気、過酸化水素、オゾン、亜酸化窒素等の窒素酸化物が存在していてもよく、無機酸素源はレーザービーム又は別個のエネルギー源で活性化されることができる。例えば、活性化された酸化ガス源、例

えば、電場を通すか又はレーザーにより活性化した酸素を、基板上の層の方向に注いでもよい。

　結晶性超伝導フィルムを成長させる場合、基板は、一般的に、約450～750℃の温度、好ましくは約500～650℃の温度に維持する。上記温度に維持することにより、原子が適切な結晶構造を形成するが、フィルムと基板の間の相互拡散を最小に抑え且つ気化によるタリウムの損失を最小に抑えるために、温度はできるだけ低く保つ必要がある。基板に使用する温度が低いほど、付着速度は遅くなければならない。又、融除プルームにプラズマを付与することにより、プルームにおける原子及び分子のエネルギーを増加することができる。このようにエネルギーを追加することにより、低温で適切な結晶構造を形成する原子の性能が増加し且つフィルムの成長速度が増加する。

　ある場合において、タリウムが高蒸気圧のために損失することがあるとき、ターゲット中のタリウムの量を増加することが好ましい。又、タリウム損失は、装置中の酸化ポテンシャルをより高く

維持することにより最少限に抑えることができる。

金属又は金属酸化物の一種又はそれらの組み合わせを順次融徐することが望ましい。この場合、異なる組成の層が順次付着し、結晶の異なる原子層が生成する。

上記した高温基板の付着の他に、熱処理の前に、室温の基板上にレーザーアブレーションを用いて付着させてもよい。室温の基板でレーザーアブレーションで形成したフィルムは、密度が大きく、均一で純度が高いが、結晶質ではない。これらの非晶質フィルムを加熱すると、液体となった後、化学処理に関して上記した方法で固体結晶性相となる。液相生成の動力学は、上記2種類のフィルムでは若干異なる。このことは、化学的に製造したフィルムは非常に多孔性である傾向があり且つ熱処理前に少量の残量炭素を含有していることによる。

上記プロセスは、異なる組成の層を用いて更に変更してもよい。特に重要なものとしては、酸化タリウム、好ましくは酸化タリウムと酸化カルシ

ウムの組み合わせからなる第一層と、少なくとも酸化銅及び酸化バリウム、好ましくは酸化タリウム及び酸化カルシウムも包含する第二層との組み合わせが挙げられる。これらの層は、上記したように、基板上に異種の組成の層を別個に設けることができる種々のプロセスを用いて得ることができる。例えば、ゾルーゲル法の場合、まず、全ての金属のカルボン酸塩の層を塗布する前に熱分解しても又はしなくてもよい、カルボン酸タリウムとカルボン酸カルシウムの層を設けることができる。

基板の塗工に関する別法としては、物理的傾斜法を用いることが挙げられる。傾斜できるボートを用いて、液体組成物を基板から離しておけるようにすることにより、種々の酸化物の液体を調製することができる。液体を生成次第、ボートを傾斜すると、ボートの他の部分に配置されている基板が液体により塗布される。この際、基板は、ボートの底に対して角度を有し、ボートの壁の近くが高部端となるように配置するのが望ましい。塗

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布を行う条件としては、迅速に約500〜880℃の範囲の温度に上昇させることが挙げられ、この時点で、酸化物は液体状態にある。次に、ボートを傾斜し、約0.5〜10℃/分の範囲の比較的遅い速度で冷却を開始し、温度が約490〜860℃の範囲のときには、少なくとも約10℃、好ましくは約50℃以下にまで降下させる。この時点で、傾斜していたボートを最初の位置に戻すと、基板はもはや液状ではなく、基板を少なくとも10℃/分、好ましくは少なくとも20℃/分で急速に室温まで冷却する。熱処理中における、ソースと超伝導体フィルムとの間の配置は、種々の形態でよい。しかしながら、ソースは、超伝導体フィルムに接触させてはならない。配置は、ソースが超伝導体フィルムと対向するようなものとする。例えば、ソースで塗布した基板は、スペーサ（一般的に、厚さが5μm以上のもの）を用いて、超伝導体フィルムで被覆した基板から離して、ソースとフィルムを対向の関係としてもよい。

別の配置として、容器中に入れた基板上に超伝

導フィルムを有する場合が挙げられ、この場合、ソースを超伝導体フィルムから移動させて、超伝導体フィルムとは異なる温度に維持する。従って、ソース温度を変えることにより、異なるタリウム超過圧力が得られ、超伝導体フィルム表面で適切なT1化学量論量が確実に得られる。

これらの超伝導フィルムの製造及び超伝導材料のポストアニーリングには、種々の方式を用いることができる。超伝導物質の生成（沈殿）の前に、フィルムにおける液体の蒸発及び沸騰を防止する加熱及び加圧の工程を設けることにより、T1ソース物質が凝縮することにより、超伝導層が沈殿して、非超伝導酸化物組成物の生成を出来るだけ抑制又は防止することができる。

このための一プロトコールとしては、約3atmの圧力とするとともに、温度を急激に（約50℃/秒の昇温速度）上昇させて、15〜20秒で室温から850℃に到達させ、超伝導フィルムをこの温度で維持する。この時点で、加熱の最初から約100秒が経過しており、その後、超伝導体を約5〜10秒間

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(34)

冷却して約550 ℃の温度とし、この温度で更に10
0 秒間維持した後、室温まで冷却する。この間に、
ソース物質に関して異なる加熱プロフィールが用
いられ、ソースは超伝導体フィルムと一緒にほぼ
同じ速度で加熱されるが、超伝導体フィルムより
も約5 〜25秒間長く高温で保たれ、その結果、超
過圧力が比較的一定に維持されるとともに、超伝
導体フィルムは最初の冷却を受け、その後、ソー
ス温度を約100 ℃だけ降下し且つ超伝導体層のア
ニーリングの間この温度で維持する。次に、超伝
導体層とともにこの温度を室温まで降下させる。
圧力プロフィールに関しては、アーリング温度に
到達後圧力を1atmに低下するまでは、高圧を維持
する。

ソースと超伝導層の両方を同じ温度に維持する
場合には、異なったプロトコールにより、約40〜
70℃/ 分で800 ℃に加熱する。この際、酸素圧力
を3atmに維持しながら、約15〜40秒、これらの約
20〜30秒で上記温度に到達させる。この高温で更
に60秒間維持後、約5 〜20℃/ 秒で室温まで温度

を降下させる。圧力プロフィールは、約60秒間高
圧を維持後、約10〜20秒で1atmまで降下させる点
で異なる。液体組成を調整することにより、1 a
tmで成長を行うことができる。

熱アニールに関するパラメータは、超伝導フィ
ルムの製造の場合とは異なる。アニールの場合、
超伝導フィルムを、約500 〜750 ℃の範囲の温度
に、一般的に約10〜30秒で急熱する。その後、タ
リウムソースの存在下で、酸素雰囲気中において
約5 〜60分間、好ましくは約15〜45分間上記温度
の±15%で維持する。ソース温度は、超伝導フィ
ルムよりも少なくとも約50℃、好ましくは約100
〜150 ℃高い。ソースは、超伝導フィルムと同様
に加熱され、ソースの最終温度は、フィルムの温
度の到達とともに、又はフィルム温度に到達直後
に達する。ソース温度を、アニールの間実質的に
一定に維持後、超伝導フィルムとほぼ同じ温度に
冷却して、ほぼ同じ速度で室温まで冷却する。こ
の際、ソースの冷却は、超伝導フィルムを冷却す
る少し前、通常約0.5 〜5 分前に開始する。アニ

(35)　　　　　　　　　　　　　　(36)

ールの間、通常約1.5 〜約2.5atm、好ましくは最
大約2atmの高圧力を使用する。

赤外線加熱を用いることにより局部効果を得る
ことができる。例えば、プレ超伝導体又は前駆体
フィルムを有する基板を、フィルム上にあって基
板よりも容積が小さい赤外線透明窓を有するエン
クロージャに入れる。赤外線加熱を用いることに
より、小容積で蒸発が生じ、圧力が急激に上昇す
る。更に、このアセンブリーを、赤外線透明窓を
有する圧力容器に入れ、アセンブリー全体を加圧
することもできる。このようにして、超伝導フィ
ルムを生成するガス環境を、酸化タリウム蒸気で
急速に飽和する。このプロセスは、大気圧又は過
圧下で行うことができる。

基板を大きなサーマルマスベース(thermal mas
s base) 上に配置し、赤外線加熱を用いることに
より、基板が前駆体又は中間液体組成物よりも熱
伝導性が大きいので、基板前駆体フィルムの界面
で熱流束が生じる。従って、フィルム及び基板に
おいて温度勾配があるので、前駆体フィルムの温

度が基板よりも高い。次に、温度の低い基板が、
超伝導体フィルムの生成の核形成部位を提供する。

本発明の理解を更に深めるために、図面を参照
して説明する。第1 図及び第2 図は、超伝導フィ
ルム製造用の管状装置及び配置を異なった図で示
したものである。金を密封した容器10には、タリ
ウムペレットソース12及び14が入っている。基板
16により、ペレット12を超伝導体層前駆体20から
分離する。ワイヤ馬テイ形スペーサ22により、ペ
レットソース14が超伝導層20に接触しないように
なっている。管10をシールする前に、種々の成分
を組み合わせて上記したようなアセンブリーを作
製してハウジング10に入れる。このハウジングを
シールして炉に入れ、所望の温度まで急激に加熱
して、その温度で維持する。しかしながら、この
プロセスの形態を用いて高品質のフィルムを製造
するのに、パウチをシールする必要はない。通常、
少量の空気又は酸素が密封ハウジング１０に残存
する。加熱すると、ペレットソースが部分的に蒸
発し、ハウジング１０において酸化タリウムの超

(37)　　　　　　　　　　　　　　(38)

過圧力を維持して、酸化タリウムが超伝導体前駆
体層から著しく蒸発するのを防止する。超伝導体
層が生成するのに十分な時間の後、炉の電源を切
って冷却し、炉のチャンバーを室温にする。

　第3 図は、別の実施態様を示したものである。
この場合、赤外線加熱を用いて所望の温度とする
ベース30の上には、導管34を有するカバー32及び
チャンバー40を排気又は加圧するためのバルブ36
が取り付けられている。カバー32には、赤外線透
明の天井42が付いており、赤外線がチャンバー40
に入るようになっている。チャンバー全体を照射
できる赤外線源44が設けられている。又、所定の
場所に配置されているときには輻射線が超伝導体
フィルム前駆体50を加熱する防止する役割を果た
す、取り外し可能なマスク46が設けられている。
超伝導体フィルム前駆体50を、ベース30の上に置
いてある基板52の上に塗布する。酸化タリウムリ
ング54を、チャンバー内の支持体56の上に取りつ
け、ここでマスクが所定の位置にあるときにタリ
ウムリングに赤外線を照射する。

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超伝導体フィルムを製造する際、超伝導体前駆
体フィルム50を塗布した基板52をベース30上に置
き、ベースにカバー32を取りつける。次に、チャ
ンバーを酸素で満たし、マスクを所定の位置に配
置して赤外線ランプ44での照射を開始する。酸化
タリウムの分圧が十分になったら、マスクを除去
し、前駆体フィルム50を高温に加熱して、超伝導
体フィルムを生成させる。十分加熱した後、ラン
プ44の電源を切り、チャンバー40を室温に冷却し、
排気し、カバーを取り外して超伝導体フィルムを
分離する。

　第4 図は、別の実施態様を示したものである。
この実施態様では、一種以上の基板を超伝導体フ
ィルム前駆体で塗布する。この場合、所望の厚さ
の層が得られるまで、繰り返し基板の塗布を行っ
てもよい。圧力ゲージ64及びバルブ66を備えた導
管62を有するハウジング60を設ける。ハウジング
60のベースには2 つのヒータ70及び72が付いてお
り、それぞれ容器74及び76に熱を提供する。容器
74の一端には、オリフィス82を介してハウジング

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60の外に延びているロッド80が付いている。シー
ル84により、空気がハウジング60に入ったり又は
蒸気が損失するのを防止している。基板86は、マ
ウント90により所定の角度で容器74内に位置させ
る。ロッド80により、容器74は、位置Aから移動
させることができる。超伝導体フィルムの液体前
駆体の表面は、ハウジング60のベース78に対して
実質的に平行である。この位置で、基板86を超伝
導体前駆体液体に浸漬する。温度を低下又は溶媒
の一部分を蒸発させることにより、基板上での超
伝導フィルムの結晶化が誘発される。ロッド80を
上げるか又は装置全体を傾斜させることにより、
点線B で示した位置92に液体を移動させることが
できる。その結果、基板86と超伝導体フィルムは、
もはや超伝導体前駆体液体94で塗布されない。容
器76には、ハウジング60において酸化タリウムの
超過圧力を提供する役割を果たすことのできる酸
化タリウム液体96が入っている。酸化タリウム液
体96は、酸化タリウム単独からなるとともに、ハ
ウジング60内の超過圧力を制御するのに用いるこ

(41)

とができるので、酸化タリウム液体96の温度は、
超伝導体前駆体液体よりは低い温度で維持しても
よい。

　目的とする装置部品は、種々の装置に用いるこ
とができる。例えば、超伝導性層はマイクロ波表
面インピーダンスが小さいので、非常に多数のマ
イクロ波及びミリメートル波の用途に用いられる。
基板及びフィルムを包含する目的とする要素は、
適当な基板を選択することにより、無線周波数キ
ャビティー及び共振器、マイクロ波シールディン
グ、アンテナ並びに同軸、マイクロストリップ、
同平面導波管、同平面ストリップライン、インバ
ーテッド又はサスペンデッドマイクロストリップ
等の異種の構造を用いた伝送線路に用いられる。
これらの装置は、信号通信又は遅延、フィルター、
共振器及びオシレータ、回路インターコネクショ
ン、パワーバインダー及びアンテナフィードに用
いられる。超伝導共振器要素を備えた狭帯域マイ
クロ波フィルターの場合、下記の仕様が可能であ
る。

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伝送媒体：マイクロストリップ結合線路
　　　　　（共振器要素：5～15）
帯域幅：中心周波数(f_o)で0.1～10%
寸法：
　　　超伝導体厚さ (t)=1 μm
　　　相対誘電率 (ε_r) =9.65(MgO)
　　　損失正接=0.0002(MgO)
　　　基板高さ(h) =25ミル
　　　間隔(s) =10～150 ミル
　　　線幅(w) =1～40ミル
　　　長さ(ℓ) 、f_oでの0.25管内波長、
　　　ℓ=114 ミル(10GH。)
パッケージ寸法：
　　　X =1 インチ
　　　Y =1 インチ
　　　Z =0.25インチ
フィルターを、遮蔽ケースに包装し、77 °K に冷却し、SMA 同軸コネクターを用いて他のハードウエア部品に接続する。
超伝導共振器要素を備えた代表的な狭帯域マイ

クロ波フィルターを第5 図に示す。このフィルターは、信号をマイクロ波フィルター102 に供給するアンテナ100 を包含している。マイクロ波フィルター102 からの信号は、信号106 と結合したミクサ104 に供給する。掃引局部オシレータ110 も、信号をミクサ104 に供給し、その結果、信号114 と結合した分散性遅延線路112 に出力が供給される。超伝導共振器要素116 が、整列した形態で示されており、「w 」が線幅であり、「s 」は間隔であり、「1 」は長さである。狭帯域マイクロ波フィルターが低損失であるので、マイクロ波受信器は比較的高い信号対ノイズ比を示すことができる。分散性遅延線路を用いて、あたかも短パルス（距離分解能がより高い）であるかのように、長パルス（より高いエネルギー）を処理する。このことについては、アールエイチ　ディッケ(R.H.Dicke)により、1953年1 月6 日発行の米国特許第2,624,876 号において最初に説明された。
　遅延線路は、デジタル瞬時周波数測定(DIFM)部品の一体部分である。遅延線路は、下記の仕様を

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とることができる。
　寸法：
　　　超伝導体厚さ (t)=0.015 μm ～2 μm
　　　ε_r =9.65(MgO)
　　　損失正接=0.0002(MgO)
　　　基板高さ(h) =25ミル
　　　線幅(w) =0.04～40ミル
　　　全長(ℓ) =20mm
　パッケージ寸法：
　　　X =1 インチ
　　　Y =1 インチ
　　　Z =0.25インチ
遅延線路を、DIFM内の遅延線路を相互接続しているSMA 同軸コネクタを用いて、77 °K の冷フィンガに熱結合した遮蔽ケースに包装することができる。
　デジタル瞬時周波数測定の略図を第6 図に示す。アンテナ120 は、信号をダイオード122 に供給する。このダイオード122 は信号をパワースプリッタ124 に供給する。パワースプリッタ124 は、超

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伝導体フィルムを包含する遅延線路134 を包含している線路130 及び132 を介して位相検出器126 に直接出力する。線路130 及び132 の出力を、位相検出器126 に供給後、信号136 及び140 をビデオ142 に出力する。

〔実施例〕
　以下、実施例により本発明を説明するが、本発明はこれらのものに限定されるものではない。
　Tl、Ca、Ba及びCu金属のカルボン酸塩化合物の各々を、確立された方法により製造した。得られた金属石鹸化合物のクロロホルム溶液を蒸発させて、体積を減少させ、原子吸光により金属含量を分析した。次に、これらの前駆体溶液を使用して、前駆体ゾルを製造した。即ち、2 －エチルヘキサン酸銅5 g、2 －エチルヘキサン酸バリウム3.29 g、2 －エチルヘキサン酸カルシウム3.14 g及びクロロホルム5 mℓに溶解した2 －エチルヘキサン酸タリウム8.462 g を混合して調製した。この前駆体の化学量論は$Tl_2Ca_2Ba_2Cu_3$であった。この

(45)　　　　　　　　　　　(46)

溶液を、数時間振盪して混合した。得られた前駆体溶液を、単結晶イットリア安定化ジルコニア（<100>配向）基板上に、4000rpm で30秒間回転塗布後、400 ℃で5 分間熱分解した。この回転／熱分解操作を250℃でさらに二回繰り返した。粉砕してせれぞれの酸化物を混合後、カーバープレスで一軸的に圧縮して、Tl：Ca：Ba：Cuのモル比が1 ：3 ：1 ：3 である酸化物ペレットを製造した。ペレットと塗工基板を、直径1/4 インチの金管に入れて空気中に置いた後密封した。密封した金管をワイヤを用いて熱電対に取りつけ、予備加熱した管炉に挿入した。物質を2 分で885 ℃の温度とし、この温度で10分間保った。次に、試料を炉から取り出し、室温に冷却した。フィルム処理操作全体が完了するのに約15分要した。

　熱分解フィルムを光学顕微鏡写真で調べたところ、フィルム全体に、多数のプレート状及び針状（端部がプレート）構造の存在が明らかとなった。エネルギー分散性X 線解析により、両方の構造が2223組成を有することが分かった。フィルムの走

査型電子顕微鏡により、超伝導2223化合物のモルホロジーを示した。又、顕微鏡写真では、プレート状構造にじかに隣接する領域に球状Ca/Tl 酸化物付着層が存在することが明らかとなった。プレートの組成を、SEM －EDX（走査型電子顕微鏡エネルギー分散X 線分光分析法）で分析したところ、12原子％のBa、12原子％のTl、12原子％のCa、20原子％のCuからなることが分かった。組成分析の結果が、面積対面積で一致し且つ物質が2223金属化学量論を有することと一致する。2223フィルムが高度に配向していることが、X 線回折スキャンにおける<001> 反射が著しく増加することから明らかとなった。又、6 ° でのピークが小さく、フィルムにおける2122層の量が非常に少ないことが分かった。物質が2 μm の厚さの密度の高いフィルムから構成されているという仮定の上で、温度依存性磁化率の測定をフィルムについて行った。計算により、物質の60％が超伝導となったことが分かった。

　ソース物質の組成がTl：Ca：Ba：Cuの原子比が

（47）

（48）

2 ：2 ：2 ：3 であることを除いて上記の操作を繰り返し、2122組成を製造した。反応温度をわずかに変えて860 ℃とした。基板としては、上記した方法〔サンワル(Sanwal)及びスタリア(Sutaria)、ジェイ マテ サイ(J. Mater. Sci.)、第11巻、2271～2282(1976)〕により化学研磨して実質的に欠陥のない(<100>) 表面とした酸化マグネシウム基板単結晶を用いた。熱分解フィルムの光学顕微鏡写真から、フィルム全体に多数のプレート状構造が存在することが明らかとなった。SEM －EDXにより、これらの構造が2122物質に相当する化学組成を有することが判明した。又、フィルムのSEM により、超伝導2122化合物が、明らかにプレート状モルホロジーを有することが分かった。更に、<001> 反射が大きく増加し、フィルムが高度にc軸配向していることが判明した。又、単結晶基板の電子チャネリングパターンをフィルムの種々の領域のものと比較したところ、フィルムがエピタキシャルであることが判明した。フィルムのモルホロジーから、処理中に中間液相が存在すること

が強く示唆された。フィルム表面（ 液相エピタキシャル成長法により得られる薄膜表面に似ている）をEDX で分析して、2122化合物が正確なカチオン化学量論量を有することが分かった。

　フィルム内の多くの代表的な領域から電子ビームチャネリングパターンが得られた。フィルムの電子チャネリングパターンから、2122フィルム内のa 、b 面の配向がフィルム全体にわたって基板の多くの領域のパターンと一致することが明らかとなった。いくつかの領域で、フィルムのチャネリングパターンが、基板とは配向が不一致（ 一定量だけ） であった。このことは、約9 ％の格子不一致により、フィルム／ 基板界面で歪み又はディスロケーションが発生したことを示しているものと思われる。表面との格子の一致は、酸化マグネシウム基板に近接した層だけでなく、基板表面から何ミクロンも離れたプレートの上部でも維持されていた。

　PVDによりタリウムを主成分とする超伝導フィルム（例えば、2 2 2 3組成を有するもの）を

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（50）

付着するには、基板を専用に設計した真空超伝導に入れ、ターゲットから約６cm離れて面する位置に配置する。真空チャンバーを１ x １０⁻⁵トルの圧力に排気後、酸素を入れて５ x １０⁻³トルに戻すとともに、基板を室温と４００ ℃の間の温度に加熱する。次に、ターゲット上でのレーザーエネルギー密度を１.５ ～２.０ ジュール/cm²として、レーザーアブレーションにより、物質をターゲットから基板に蒸気輸送する。レーザーを５Hz で５ ～１０分間パルス化して、厚さ０.５ ～１.０ μm のフィルムを付着させる。アブレーションの後、フィルムを室温に冷却し、基板を真空チャンバーから取り出す。 このように付着させたフィルムは連続しており、基板全体にわたって平滑である。フィルム表面上のある位置には、固体粒子又は小さな融解小球の形態でターゲットから輸送されたと思われる粒子がある。エネルギー分散性X 線(EDX) 分光分析法により測定すると、４００ ℃以下の基板温度では、フィルム組成は、ターゲット組成と同じであることが判明する。即ち、ターゲットが2223

組成を有している場合、フィルムはそれと同じ組成を有している。基板温度が６００ ℃であるとき、タリウムが蒸発により損失するので、フィルムの最大含量は、基板の最大含量よりも小さい。この損失は、ターゲットのタリウム含量を増加することにより補うことができる。

フィルムは、付着させたままではでは超伝導性ではなく、タリウム蒸気源をの入った金パウチ内で７５０ ～８５０ ℃でアニールすると超伝導性となる。

更に、種々の基板を用いて多数の超伝導体フィルムの製造を行った。基板としては、多結晶形態の酸化マグネシウム、ジルコニア及びアルミナだけでなく単結晶サファイアが挙げられる。Tl、Ca、Ba及びCuの2 －エチルヘキサン酸塩のクロロホルム溶液を基板に塗布後、得られるフィルムを250 ℃で熱分解してフィルムを製造する。このプロセスを最高10回以上繰り返して所望の厚さとした後に高温処理する。基板の塗布を3 回繰り返した後のフィルム厚さは5 μm である。

まず清浄基板を上記したようにして3 回塗布し

(51)　　　　　　　　　　　　　　　　　(52)

して化学付着フィルムを製造する。予備熱分解したフィルムは、XRD 及びTEM により非晶質であることが分かる。このフィルムは、金属イオンの均質混合物であり、高温熱分解前のTl 、Ca化学量論量は、高温超伝導体(HTSC) 物質を製造する上で特に重要ではないことが判明した。しかしながら、過剰のBa及びCuを添加すると、高温熱分解の間に、バリウムキュプラートの大きな六方晶が生じる。

下記の操作により高温熱分解処理を行う。最初に非晶質化学付着させたフィルムを、2 つのソースペレットの間に配置する。ソース物質は、一般的に、直径1/2 インチのTl－Ca－Ba－Cu酸化物の一軸圧縮粉である。ソース物質の化学量論量は、処理中に生成する相を決定するのに重要な役割を果たす。使用するソース組成物でもっとも普通のものは、Tl－Ca－Ba－Cu比が1313及び2223のものである。スペーサを、ペレットとそれらの間に挿入したフィルムの間に配置する。セラミック又は金属スペーサを用いることにより、フィルム表面がペレットの表面に触れるのが防止される。フィ

ルムとソース物質との接触を防止するのは、大きな領域（> 1 cm²）にわたって形態学的に均一なフィルムを得るのに重要である。フィルムかソース物質と接触すると、焼成した最終フィルムの均一性及び一体性が損なわれることがある。

ソース/ フィルム構造体を、予め条件を整えた金管に挿入する。次に、金管を空気、窒素又は酸素でパージし、ふたをする（ 気密シールをする必要はない）。その後、600 ～910 ℃の最終温度に加熱する。この際、用いる加熱速度が重要である。加熱速度が遅くて10～30℃/ 分の範囲であると、通常、厚さ2 ～10μm の多結晶無配向フィルムが生成する。一方、加熱速度がもっと早いと、配向フィルムが生成する。配向フィルムを生成するのに使用する典型的な加熱速度は、50～500 ℃である。金のパウチを予備加熱した管炉に直接入れ、パウチに直接挿入した熱分解電対を用いてその温度を監視することにより、加熱速度をもっと高めることができる。化学付着したフィルムを急熱して得られるフィルムの配向は、基板表面に垂直な

(53)　　　　　　　　　　　　　　　　　(54)

物質のc 軸である。このような物質の場合、0.3゜のシャープなロッキングカーブが得られた。基板に平行なc 軸を有する物質の核形成を示すある確証が得られたが、この物質は、いずれのフィルムでも占める容積割合が小さい。単結晶MgO 基板では、エピタキシーが示された。

フィルムの配向度は、本質的に相生成プロセスに関連している。高温処理中に得られる中間液相は、モホロジー、相密度及び純度、結晶配向並びにフィルムの密度を制御する上で重要な役割を果たす。検討したところ、得られる中間液相は低温（約600℃）では主にTl及びCaの酸化物からなることが分かった。急熱試料の場合、650℃の低温で、2層物質の大きな結晶粒子が観察された。このことは、これらの比較的低い温度で液相生成が実際に生じていることを示している。熱分解化学前駆体のDSC実験により、これらの知見が裏付けられる。加熱速度が遅いと（即ち、10℃／分）、フィルムにおいて比較的少量の液相（単位容積当たり）及びフィルム内に多数の核形

(55)

成部位が生じる。これらのことが合わさって、結晶配向が非常に低い微細な結晶粒子物質（<5 μm）が生成する。核形成の方向性はランダムであり、付着層全体に発生し、超伝導物質のランダムに相互接続した小さな板状構造が生じる。フィルムが5 μm 粒子物質のかなり多孔質な網状構造を有していることは別として、基板へのフィルムの付着量は良好で均一である。単結晶MgO 上に設けた多結晶フィルムの表面抵抗を測定したところ、この物質は、損失がかなり低く、50 °K 及び10GHz で、極低温銅よりも表面インピーダンスが約2 倍以上大きいことが分かった。

一方、加熱速度が大きいと（>50℃／分）、著しく異なるフィルムモルホロジーが生じる。前駆体フィルムの急熱中に、大きな容積において液相が生成する。最初は主にTl及びCaの酸化物からなるこの液体は、バリウム及び銅と接触して急速にそれらを溶解して、2122又は2223化合物を直接沈殿する。この液相は非常に流動性があって、加熱工程の初期に生成する。この中間液相を介した物質

(56)

輸送は極めて迅速である。従って、最初に多孔質で5 μm （低初期密度）の厚さのフィルムは厚み方向に収縮して、処理中に1 μm よりも少し大きい厚さとなる。液体から生じる相は、液体と平衡である超過圧力によって異なる。2223相を含有する（又はアニール処理中に2223相を生成する）ソース物質を用いると、一般的に、2223相を含有するフィルムが生じる。局部タリウム超過圧力は、液体から生成する相を決定する上で重要である。超過圧力が低すぎると、超伝導物質は得られない。結晶配向度は、フィルム処理条件を適切に選択することにより容易に制御できる。加熱速度を20～50℃／分（最終形態は、多結晶及び配向／エピタキシャルフィルム成長）とすると、ある範囲のモルホロジー、密度及び厚さを有する部分配向フィルムが得られる。抵抗率測定（107 °K でR ＝0）及びAC感受性の両方により、2 層フィルムの場合に、シャープな超伝導転移が得られた。単結晶MgO 上に本方法により生成した配向2122フィルムは、従来報告されたいずれのHTC フィルム又はバルク材

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料よりも、77 °K での表面抵抗が低いことは明白である。この物質は配向しており、基板とはエピタキシャルな関係にあると思われる。同じ処理パラメータを用いて作製したフィルムは、非常にシャープなX 線ロッキングカーブ〔一般的に、半値全幅(FWHM)が0.7 ゜未満〕を示すことが判明した。0.3 ゜の低い値も得られた。この値は、いずれの物質から得られたHTSC薄膜に関して報告されているロッキングカーブの中でも最も優れたものに匹敵する。更に、このプロセスを最適化することにより、更なる改善が可能である。

Tlオーバーコートを有するフィルムの急速サーマルアニールに関して、下記の実験を行った。2-エチルヘキサン酸タリウムを、Ca、Ba及びCuの酸化物を含有する予め固定したフィルム上に回転塗布した。上記第一フィルムは、Tlが試料から完全に蒸発するのを防止するに十分なTl超過圧力過で、通常の化学量論フィルム(2223)を焼成することにより製造した。合計3 つのTlオーバーコートを追加後、密閉金パウチ内において、酸素雰囲気

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中860 ℃で焼成した。ソースペレットをパウチに入れてT1超過圧力を制御した。処理後のフィルムは、多量の3 層超伝導物質を含有していた。

　次の実験において、適当な金属カチオンの2223混合物を硝酸に溶解し、この溶液を単結晶MgO 基板上で蒸発させた。この物質をボックス炉において、80℃で乾燥し、金パウチ中で、通常の操作を用いて焼成した。熱処理した硝酸塩前駆体から2122化合物が生成した。フィルムの多数の部分のモルホロジー及び組成は(SEM−EDX) 、2122物質の存在と完全に一致した。前駆体フィルムを付着するのに使用することができる他の溶液又はコロイド状分散液としては、これらの金属イオンの炭酸塩、クエン酸塩、水酸化物、フッ化物、塩化物及び酢酸塩が挙げられる。T1、Ca、Ba又はCu塩は、同一の対イオン(即ち、全てが塩化物) を共有してもよいし、又は異種のアニオンの種々の錯体混合物からなっていてもよい。前駆体は、相生成及び対イオンの除去を完全に行うのに適当な条件下(即ち、ハロゲン化物の除去には、含水雰囲気、有機

物の場合には酸素雰囲気下で加熱する必要がある)で焼成される。

　検討の結果、フィルムのモルホロジー及び性質の設計に使用する中間液相が、技術的に重要な種々の物質と非常に反応性があることが分かった。フィルム内に生成した部分融解物を直接に物理的接触すると、超伝導物質が崩壊する場合がある。基板がサファイア又は多結晶アミナ等の場合には特にこの傾向がある。A1含有基板状に設けたフィルムを処理した後、フィルム中にバリウム−アルミネート結晶の存在が観察されることがあった。又、熱処理の初期に生成し、その後物質を崩壊するための処理中に液体と接触して溶解した、2122又は2223化合物の単結晶板の腐食が明らかに認められた。

　下記の手法を用いることにより、基板からの妨害のない状態で、サファイア基板上に超伝導T1フィルムが生成される。まず、中間の加熱速度(約50℃/ 分) を用いてフィルムを焼成する。この加熱速度では、処理中のいずれの時間であっても、

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存在する液相の量を効果的に制限する役割を果たす。第二に、物質が高温状態にある時間を減少させることにより、基板の反応を制限する。これらの手法の両方とも、研究室において、サファイア基板上での2122又は2223相と基板との好ましくない反応をうまく抑制できることが明らかになった。

　温度の低下又は高温での時間の短縮以外に、基板反応を減少させる別の方法として、トラブルを起こしやすい基板材料の上にバリヤー層を設けることが挙げられる。例えば、サファイア、シリコン及びヒ化ガリウム基板の場合には、緩衝層としてMgO 及びイットリア安定化ジルコニアを用いることができる。ジルコニア(イットリア安定化) 及び酸化マグネシウムは、意図する通常の処理条件下で、上記物質と相の適合性を示した。

　下記の実験操作を用いて、多数の超伝導体フィルムの製造を行った。

　公表されている標準の合成法により、2 −エチルヘキサン酸の金属塩を製造した。2 −エチルヘキサン酸銅、2 −エチルヘキサン酸バリウム、2

−エチルヘキサン酸カルシウム及び2 −エチルヘキサン酸タリウムから調製した溶液を、適当な基板上に回転塗布してフィルム自体を生成した。フィルムの厚さは、溶液粘度、回転速度、回転時間及び塗布の回数を制御することにより調整した。一般的には、基板を3000rpm で30秒間回転した。各前駆体の塗布の後、フィルムを250 ℃で6 分間焼成して2 −エチルヘキサン酸塩を熱分解する。これを3 回繰り返して、前駆体物質の厚さを十分なものとする。

　熱分解したフィルムを、公知の化学量論(例えば、T1/1:Ca/3:Ba/1:Cu/3)を有する酸化物ペレットが入っていて且つ圧縮シールした金パウチに入れた。空気及び酸素雰囲気の両方により、超伝導相がうまく生成した。装入した金カプセルを、水平管炉において、750 ℃〜920 ℃の範囲の温度で30秒〜5 分間加熱した。この場合、全ての試料について、粉末X 線回折及びエネルギー分散性X 線解析により、超伝導相が確認された。

　以下、一般的な実験操作の概要を説明する。

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最小容積のクロロホルム中で、2−エチルヘキ
サン酸銅5 g 、、2−エチルヘキサン酸バリウム
3.29 g 、2−エチルヘキサン酸カルシウム3.14 g
及び2−エチルヘキサン酸タリウム8.462 g を、
数時間振盪して混合した。この前駆体溶液を、1
x 1 cmの単結晶イットリア安定化ジルコニア(>10
0<配向) 基板上に、3000rpm で30秒間回転塗布し
た後、リンドベルグ(Lindberg)ボックス炉中で25
0 ℃で6 分間熱分解した。この回転塗布/ 熱分解
操作を、250 ℃で更に2 回繰り返した。塗工基板
及びTl:Ca:Ba:Cu のモル比が1:3:1:3 である酸化
物ペレットを、空気雰囲気下で金パウチに入れた。
フィルムを2 つのペレットの間に挟み、熱電対ワ
イヤから作製したスペーサを用いて、フィルム表
面がペレット自体から離れた状態となるようにし
た。このパッケージ全体を、リンドベルグ1 イン
チ管炉で加熱して、10 分間で25℃から855
℃の温度とし、この温度で4 分間維持した。炉を
開いて室温まで冷却した(所要時間5 分)。

レーザーアブレーションの利点としては、真空

蒸着に固有の清浄性があること；フィルム成長速
度の正確で且つ繰り返し制御することが可能であ
ること；ターゲット組成によりフィルムの化学量
論量を制御できること；酸素種の選択及び/又は
プラズマ活性化により酸素活性が制御できること；
並びに高温で基板上に成長できるのでエピタキシ
ャル成長が促進されることが挙げられる。

〔発明の効果〕

結晶性基板上に設けた超伝導性タリウムを主成
分とする層を包含する本発明の物品は、従来製造
された物質と比較して非常に改善されている。又、
本発明の物品は、液体窒素又はそれ以上の温度で
超伝導性を有し、高度に配向しており、多くの場
合結晶性基板上にエピタキシャル成長でき、又、
上記したように、多数の非常に望ましい物理的且
つ電気的な性質を有している。

更に、本発明によれば、超伝導体組成物を製造
するための新規な方法が提供される。本発明の製
造方法では、高度に配向したエピタキシャルフィ

ルムが生成するように、成長を綿密に制御できる。
更に、均質性及び均一性に優れたゾルーゲルフィ
ルムが得られるように、厚さを制御できる。又、
温度条件を制御することにより、結晶成長速度が
制御され、実質的に均質となる。

ゾルーゲル法の利点としては、大きな領域を均
一に塗布できること；室温で成分を原子的規模で
混合できること；混合金属酸化物を低温で合成で
きること；粉末、バルク、フィルム又は繊維とす
るのに容易であること；並びに高い化学純度で得
ることができることが挙げられる。

レーザーアブレーションシステムには、安全で
あること；システムを室温で開放できること；現
場で超伝導Tlフィルムを製造するのに適している
こと；アブレーション及び凝縮帯域を使い捨てシ
ールドにより囲むことができるので、ストレイタ
リウムを付着でき、成長速度及び厚さを慎重に制
御でき及びエピタキシャル成長が促進されること
が挙げられる。

本発明により、超伝導性を有する種々の厚さの

フィルムを製造する多数のプロトコールが提供さ
れる。本発明の方法は、簡便であり、種々の基板
の被覆ができ、種々の物理的特性の超伝導性フィ
ルムを生成できる。

本明細書において言及した全ての刊行物及び特
許の開示内容は、本発明に利用できる。

上記において、本発明を、図面及び理解を深め
るために実施例によりある程度詳細に説明した
が、特許請求の範囲の精神及びその範囲から逸脱
することなく、ある程度の変更及び修正が可能で
あることは、当業者にとっては容易に理解できる
ことであろう。

4. 図面の簡単な説明

第1 図は超伝導体フィルム製造用の密封容器ア
センブリーの略側面図であり、第2 図は第1 図の
線2 −2 についての断面図であり、第3 図は超伝
導体フィルムを製造するために赤外線加熱を利用
した装置を用いた別の実施態様を示したものであ
り、第4 図は基板を超伝導体フィルムで塗布する
ために傾斜容器を用いた別の実施態様の略図であ

り、第5 図は狭帯マイクロ波フィルターの概略図
であり、第6 図はデジタル瞬時周波数測定装置の
概略図である。

10・・・容器、
12,14・・・タリウムペレットソース、
20・・・超伝導体前駆体、
22・・・スペーサ、
30,78・・・ベース、
32・・・カバー、
34・・・導管、
40・・・チャンバー、
42・・・赤外線透明天井、
44・・・赤外線ランプ、
46・・・マスク、
50・・・超伝導体フィルム前駆体、
52,86・・・基板、
56・・・支持体、
60・・・ハウジング、
70,72・・・ヒータ、
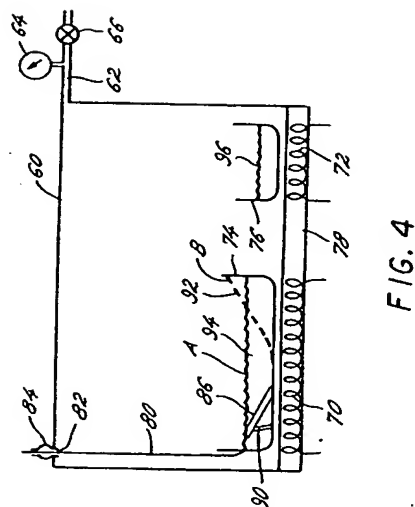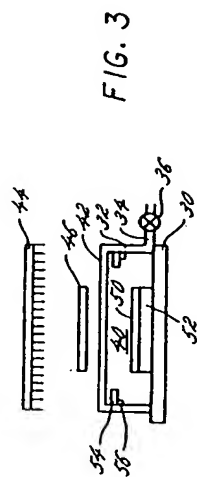80・・・ロッド、

84・・・シール、
94・・・超伝導体前駆体液体、
96・・・酸化タリウム液体。

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　弁理士　西　山　雅　也

(67)

(68)

FIG. 2

FIG. 1

FIG. 3

FIG. 4

アンテナ

マイクロ波受信器

アンテナ 100

マイクロ波
フィルター 102

ミクサ

104 分散性
遅延線路 112

108

114

110 掃引局部
オシレータ

ナイキストデータレート
での出力幅/
周波数/タイムシグナル
スペクトル

W

W 118

S

116

α　α　α　α

SMA 同軸コネクタ

FIG. 5

アンテナ

デジタル瞬時周波数測定（DIFM）

アンテナ 120　122

パワー
スプリッタ 124　132

130 位相
検出器

136 HI
140 ⅦI
VIOC

134　136

遅延線路

遅延線路

134
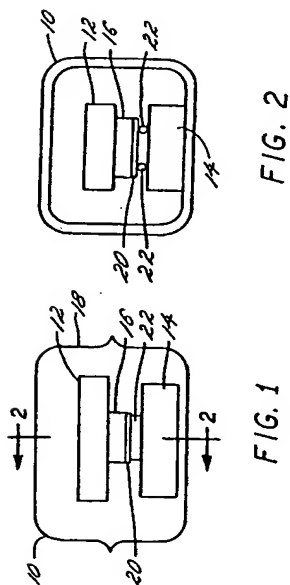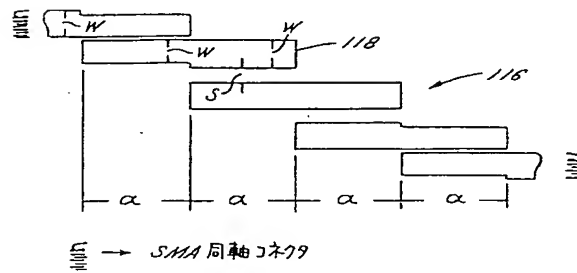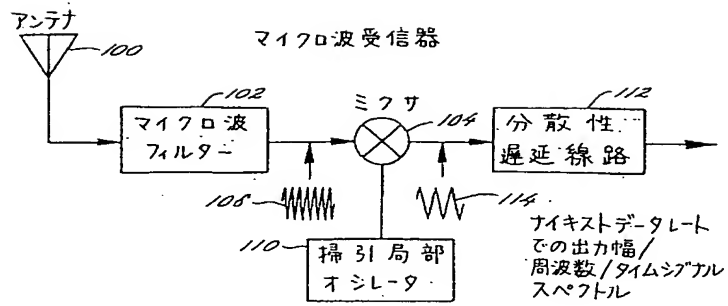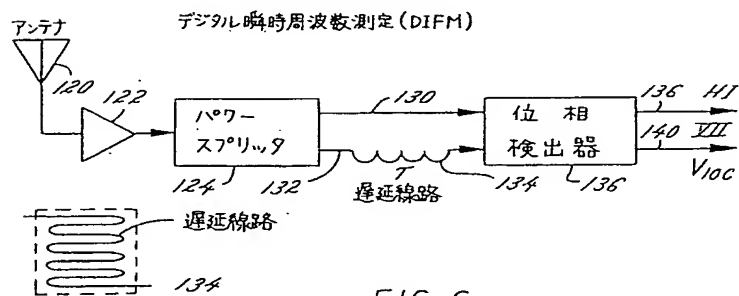
FIG. 6

第1頁の続き

⑤Int. Cl.⁵		識別記号	庁内整理番号
H 01 B	13/00	HCU Z	7364－5G
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	11/00	ZAA F	7741－5J

優先権主張　㉜1989年2月8日㉝米国（US）㉛308149

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⑫発　明　者	ロバート　ビー．ハモンド	アメリカ合衆国，カリフオルニア　93109，サンタ　バーバラ，メサ　レイン　309

【公報種別】特許法第17条の2の規定による補正の掲載
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H01P	3/08	ZAA
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【FI】

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H01B	12/06	ZAA 4232-5L
	13/00	HCU Z 7244-5L
H01L	39/02	ZAA B 8832-4M
H01P	3/08	ZAA 4241-5J
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手続補正書

平成8年7月7日

特許庁長官　荒井寿光殿
1. 事件の表示
　　平成1年特許願第221843号
2. 補正をする者
　　事件との関係　　　　　特許出願人

　　名称　スーパーコンダクター　テクノロジーズ　インコーポレイティド

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　　氏名　弁理士（7751）石田　敬
4. 補正の対象
　(1) 明細書の「発明の名称」の欄
　(2) 明細書の「特許請求の範囲」の欄
　(3) 明細書の「発明の詳細な説明」の欄
5. 補正の内容
　(1) 明細書の「発明の名称」を下記のとおり補正する。
　　・「超伝導体及びマイクロ波又はミリ波装置」
　(2) 明細書の「特許請求の範囲」を別紙のとおりに補正する。
　(3) 明細書の「発明の詳細な説明」の欄
　　（イ）明細書第9頁第3〜5行、「の製造方法、得られる組成物及びこのような組成物」を「及びこれ」と補正する。
　　（ロ）同第13頁第13行、第14頁第5行、「ミリメータ波」を「ミリ波」と補

正する。
　　（ハ）同第11頁第6行、第12頁第1、第4行、第15頁第11、第13、第13〜14、第14、第15、第16（2か所）、第17〜18行、第16頁第2、第4、第8、第9行、第45頁第14行、第56頁第10行、第57頁第16行、第58頁第1行、「°K」を「K」と補正する。
　　（ニ）同第16頁第6行、第42頁第7行、「ミリメートル波」を「ミリ波」と補正する。
　　（ホ）同第34頁第9行、「比澱」を「沈澱」と補正する。
　　（ヘ）同第43頁第8行、第45頁第6行、「25ミル」の次に「（64×10⁻³cm）」を加入する。
　　（ト）同第43頁第9行、「10〜150ミル」の次に「（25×10⁻³〜 380×10⁻³cm）」を加入する。
　　（チ）同第43頁第10行、「1〜40ミル」の次に「（2.5×10⁻³〜 100×10⁻³cm）」を加入する。
　　（リ）同第43頁第14、15行、第45頁第10、11行、第63頁第16〜17行、「1インチ」の次に「（2.5cm）」を加入する。
　　（ヌ）同第43頁第18行、第45頁第12行、「0.25インチ」の次に「（0.64cm）」を加入する。
　　（ル）同第45頁第7行、「0.04〜40ミル」の次に「（0.1×10⁻³〜 100×10⁻³cm）」を加入する。
　　（ヲ）同第47頁第9行、「1／4インチ」の次に「（0.64cm）」を加入する。
　　（ワ）同第53頁第12行、「1／2インチ」の次に「（1.27cm）」を加入する。
　　（カ）同第55頁第9行、「モホロジー」を「モルホロジー」と補正する。
　　（ヨ）同第64頁第9〜10行、「超伝導性タリウムを主成分とする」を「タリウムを主成分とする超伝導性」と補正する。
6. 添付書類の目録
　　　特許請求の範囲　　　　　　　　　　1通

2．特許請求の範囲

1．結晶基板上に、タリウム、任意成分としてのカルシウム、バリウム及び銅の酸化物からなる配向エピタキシャル成長超伝導層を有する超伝導体であって、前記超伝導層は厚さが少なくとも30Åであり、c軸が結晶基板に垂直に配向し、かつ前記超伝導層のa軸およびb軸が基板に対して一定の関係にあるように基板に対してエピタキシャル成長された超伝導体。

2．前記超伝導層が、2122組成を有する、請求項1に記載の超伝導体。

3．前記超伝導層が、2223組成を有する、請求項1に記載の超伝導体。

4．前記基板が、酸化マグネシウムまたはイットリア安定化ジルコニアである、請求項1に記載の超伝導体。

5．前記超伝導層の、厚さが2μm以下である、請求項1に記載の超伝導体。

6．前記結晶基板は、単結晶からなる、請求項1に記載の超伝導体。

7．前記結晶基板は、アルミン酸ランタンまたはサファイアである、請求項1に記載の超伝導体。

8．前記超伝導層は、この層のa軸およびb軸の方向において、最小の寸法が少なくとも3cmである、請求項1に記載の超伝導体。

9．前記超伝導層は、この層のa軸およびb軸の方向において、最小の寸法が少なくとも5cmである、請求項8に記載の超伝導体。

10．表面抵抗が、約77Kにおいて、10GHzで10⁻³オーム以下である、請求項1に記載の超伝導体。

11．表面抵抗が、約77Kにおいて、10GHzで10⁻⁴オーム以下である、請求項10に記載の超伝導体。

12．前記エピタキシャル成長層は、この層のaおよびbの方向における最小の寸法が、少なくとも0.5cmである請求項1に記載の超伝導体。

13．酸化マグネシウム上に、タリウム、バリウム、カルシウムおよび銅の酸化物の超伝導エピタキシャル層を有する超伝導体であって、前記層が、基板にエピタキシャル成長しており、かつ前記層のa軸及びb軸が基板に対して一定の関係にあることを特徴とする超伝導体。

14．前記超伝導層が、2122組成を有する、請求項13に記載の超伝導体。

15．前記超伝導層の厚さが約1μm未満である、請求項1、13および14のいずれかに記載の超伝導体を有するマイクロ波またはミリ波の装置。

16．前記装置が共振器を含む、請求項15に記載のマイクロ波またはミリ波の装置。

17．前記装置が、遅延線を含む、請求項15に記載のマイクロ波またはミリ波の装置。

EUROPEAN PATENT APPLICATION

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The title of the invention has been amended (Guidelines for Examination in the EPO, A-III, 7.3).

(54) Superconducting article containing thallium, and method for producing the same.

(57) Methods, compositions and devices are provided employing thallium superconducting layers on crystalline substrates. The superconducting layers are formed in a variety of ways, particularly by metal carboxylate pyrolysis or ablation followed by thermal annealing. Microwave and millimeter wave devices are described.

EP 0 357 507 A2

Description

LIQUID PHASE THALLIUM PROCESSING AND SUPERCONDUCTING PRODUCTS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of Application Serial No. 238,919, filed August 31, 1988.

INTRODUCTION

Technical Field

This invention concerns processes for producing thallium based superconductors, the resulting compositions, and devices employing such compositions.

Background

A recent scientific revolution in high temperature superconductivity has resulted from the discovery of many new metal oxide compounds, particularly copper oxide compounds, having dramatically increased superconducting transition temperatures (T_c). The initially discovered compounds were, for the most part, based on the combination of alkaline earth metals and rare earth metals, such as barium and yttrium in conjunction with copper. More recently, thallium based superconductors have been prepared, where the compositions have various stoichiometries of thallium, calcium, barium, copper and oxygen. The thallium materials have been more difficult to process, since the thallium Ca-Ba-Cu-O deposits are able to attain a composition which is liquid at processing temperatures. Thallium oxides have a relatively high vapor pressure at processing temperatures about 500°C and this has added to the difficulties in processing to ensure that the crystal structure has the correct stoichiometry. For the most part, sealed Au or Pt ampoules are used to control Tl volatilization by developing a controlled overpressure of Tl and oxygen above the film during high temperature processing.

Superconducting films are of great interest. However, in order to be useful, the films must be fairly uniform, be capable of carrying the current requirements of the device, have a superconducting transition temperature desirably substantially greater than the temperature of liquid nitrogen, have much lower RF surface resistance than copper, and be capable of reproducible preparation.

Relevant Literature

Ginley and co-workers at Sandia National Laboratories recently reported the preparation of superconducting thin films of the 2122 thallium compound (Tl_2,Ca,Ba_2,Cu_2,O_8). Jim Kwak at the same laboratory has reported polycrystalline thallium based films on yttria stabilized zirconia. Their films were prepared on yttria stabilized zirconia substrates by sequential e-beam evaporation of the individual metals on the substrate, followed by a post deposition reaction step in a closed platinum crucible. The films that were obtained were unoriented and exhibited a transition temperature of 97K. IBM has reported preparing oriented thin films of the 2223 and 2122 compounds by rf diode sputtering.

A large number of articles have been published concerned with the thallium compounds. Illustrative of these articles are Sheng and Hermann, Nature, (1988) 332:55-58; Sheng and Hermann, Nature, (1988) 332:138-139; Ginley et al., Physica C, (1988) 152:217-222; Superconductor Week, Vol. 2, No. 18, May 9, 1988, reported that Sandia had prepared unoriented polycrystalline TL thin films that have reached critical current densities of 110,000 A/cm² at 77K with a T_c at 97K. In the presence of a high magnetic field (6 Tesla), a critical current density of 1 x 10⁶ A/cm² at 4K was observed.

Venkatesan et al., Appl. Phys. Lett. (1988) 52:1193-1195, and Wu et al., Proceedings of SPIE Symposium on High T_c Superconductors, Newport Beach, CA March 1988, report the use of pulsed laser deposition for preparation of high T_c superconducting thin films. Venkatesan et al., and Wu et al., supra claim to have achieved YBaCuO films that are superconducting after deposition at 650°C, followed by oxygen annealing at 450°C. Witanachchi et al., (Appl. Phys. Lett., in press) report that with the addition of DC bias plasma during laser ablation of high T_c superconducting YBaCuO thin films, in situ superconducting films can be achieved at substrate temperatures as low as 400°C.

SUMMARY OF THE INVENTION

Superconducting thallium based films on substrates are provided, employing processes using growth from a liquid phase onto a crystalline substrate. Various techniques and conditions are provided to produce crystalline layers of superconductive material onto the substrate, obtaining epitaxial growth in some instances. The products have superior superconductive properties as evidenced by surface impedance, with the products finding particular applications as components of electronic devices for microwave and millimeter wave applications.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagrammatic side view of a sealed vessel assembly for production of a superconductor film;

Fig. 2 is a cross section view along lines 2-2 of Fig. 1;

Fig. 3 is an alternate embodiment employing a device using infrared heat to produce a superconductor film;

Fig.4 is a diagrammatic view of an alternate embodiment using a tilting vessel for coating a substrate with a superconductor film;

Fig. 5 is a schematic view of a narrow band microwave filter; and

Fig. 6 is a schematic view of a digital instantaneous frequency measurement device.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

Methods, compositions and devices are provided comprising a thin film thallium based superconductor composition. The compositions comprise an average composition Tl_a Ca_{n-1}, Ba_2 Cu_n O_{2n+4} as films on a variety of substrates, particularly crystalline substrates. Methods which have been employed to produce the films are both chemical and physical deposition techniques and include sol-gel and laser ablation techniques as preferred. The superconductor layer coated substrates find use as components in a wide variety of electronic devices, particularly with microwave and millimeter wave applications.

The films which are provided are primarily thallium-(calcium)-barium-copper oxides, with a stoichiometry which may include 2021, 2122, 2223, or such other stoichiometries as may be employed. The films will be oriented films, so as to have a substantially uniform crystallinity. The films may be comprised of a single crystal or a plurality of crystals joined at their grain boundaries. The films will be highly oriented with the c-axis substantially normal to the surface of the substrate as demonstrated by X-ray analysis or electron beam channeling techniques. For the most part, single phase films will be obtained, although, as desired, mixtures of two of the phases or related phases may be achieved within the film. For some applications polycrystalline films may be prepared.

The thickness of the film may be controlled. The film may be as thin as one layer, where the layer includes all of the necessary planes to obtain superconductivity, generally from about 30-50 °A, or may be as thick as two micrometers or greater, depending upon the particular application. The thickness of the film is primarily a practical consideration, rather than a significant limitation of the procedures employed.

For many uses, a fraction of a micrometer thickness will be employed, generally in the range of about 0.1 - 1 μm. The film will have a superconducting transition temperature of at least 75K, more usually 90K, preferably at least about 100K, more preferably about 115K, and particularly preferred at least about 122K, where the transition temperature has so far been substantially less than about 150K. 2122 composition films can be achieved with a T_c of at least 110K and 2223 films with a T_c of at least 122K. The superconducting transition temperature should be as high as feasible, though in some situations one parameter may be compromised for another parameter. For the most part the films will be used at temperatures in the range of about 60 - 100K.

The films will usually have critical current densities at 77K of at least about 10^3 A/cm^2, usually at least about 10^6 A/cm^2. For microwave and millimeter wave applications, the surface resistance or impedance will generally be less than about $10^{-3}\Omega$, more usually less than about $10^{-4}\Omega$, at 10 GHz and at a temperature above 50K, preferably above about 75K.

The films will be substantially free of contaminants, having less than about 10 wt. %, preferably less than about 5 wt. % of material not involved with the superconducting crystal. For the most part, films will be at least about 0.5 cm as their smallest dimension and 3 cm or as large as 5 cm or more as their smallest dimension in the a,b plane.

The films will be of high quality, as demonstrated by low lattice fault densities. By low lattice fault density is intended a sufficiently low fault density to demonstrate the intrinsic superconducting physical transport properties and sufficient to achieve required device property requirements. In addition, smooth surface morphologies can be achieved as well as uniform thickness. See Forsyth, Science (1988) 242:391-399, for a description of surface morphology of Nb_3Sn superconductors and the effect on electromagnetic properties.

Furthermore, the films may be grown epitaxially on substrates, where the crystal lattice of the superconductor does not differ by more than about 10% from that of the substrate. That is, along the a-axis of the crystal, the difference in lattice parameter between their a axes $((a_{substrate}-a_{superconductor})^a/_{substrate})$ may differ by up to about 10% and still obtain epitaxial growth. Epitaxy is desirable but is not required to obtain highly oriented c-axis normal films. However, with the subject film in addition to being highly oriented, one may also achieve epitaxy by appropriate choice of substrate.

Epitaxial Tl 2223 and 2122 films on {100} surfaces of MgO having intentional deviations of a few degrees from nominal orientation on axis can be beneficial. In a Tl 2223 film the <001> axis (lattice parameter, c = 36.26 A) is substantially coincident with the <001> axis of the MgO substrate or is at a systematic angular deviation in epitaxy with large lattice mismatches. Besides the correlation of the <001> axes, the epitaxial Tl film has its <100> and <010> axes parallel or at a systematic deviation to the analogous axes of the MgO substrate.

Various substrates including single crystal, polycrystalline, and amorphous substrates may be employed, depending upon the particular use for the coated substrate, whether one wishes epitaxy, the particular processing conditions, and the like. Substrates which may find use include magnesium oxide, yttria stabilized zirconia, sapphire, alumina, silicon, lanthanum aluminate, strontium titanate, gallium arsenide, lanthanum gallate, and calcium fluoride.

Various techniques may be employed for producing thallium based superconductors on a solid substrate. Techniques which have been employed in the past with other superconductor metal oxide compositions include laser ablation, thermal evaporation, liquid phase epitaxy, electron beam, magnetron sputtering, and chemical vapor deposition. Illustrative of methods for producing the subject

epitaxial layers are liquid phase thermal processing of sol-gel coating and laser ablation deposited coating.

Liquid phase film formation involves heating a deposited film to form a liquid coat on a substrate, whereupon the metal oxides crystallize from the liquid onto the substrate to form the superconductor layer. A liquid composition can be formed with Tl oxide, by itself or in combination with calcium oxide, as the solvent, with the other oxides becoming dissolved in the Tl oxide-containing liquid at an elevated temperature and subsequently crystallizing with the correct stoichiometry. Upon cooling, evaporation of the solvent, or chemical precipitation, the metal oxides crystallize to form a crystalline superconductor layer. Depending upon the substrate, the layer may also be epitaxial. One need not use the oxides initially, but can use metal compounds which may serve as the source of the metals in the liquid phase, where the counterions and conditions result in the formation of the desired oxide. The process may be divided into the following components: (1) Coating of the substrate; (2) Environment during crystallization; and (3) Thermal process conditions such as temperature, pressure, time; and (4) Miscellaneous other considerations.

For epitaxial growth, there will have to be pretreatment of the substrate to achieve consistent results. The liquid phase epitaxial procedure employs highly polished surfaces of the substrate. The surface may be polished mechanically or chemically, preferably both. Single crystal substrates are employed to obtain epitaxial film structures. For example, single crystal magnesium oxide <100> may be polished using hot concentrated phosphoric acid, for example, at about 80°C with 85% phosphoric acid for 10 min, or by lapping the surface flat and to the desired orientation and then immersing in conc. phosphoric acid at 50°C for 1-3 min. The resulting chemically polished crystal surface should be very clean, and provide a substantially defect free surface. The particular manner in which the surface is polished is not critical to this invention. Desirably, as exemplary of magnesium oxide, the (100) plane surface will be employed.

Coating of the substrate may be achieved in a variety of ways. One technique is to use chemical precursors, which upon pyrolysis may provide the desired oxide as a coating. Another technique is to employ a liquid comprising a solution of the metal oxides having an appropriate stoichiometry for production of the superconductor. Other techniques have been indicated, which involve vapor phase deposition. The first technique to be considered will be employing metallo-organic precursors to produce. the oxides.

A sol composition is prepared employing metal soaps providing for the appropriate stoichiometry. The soaps will be carboxylates of at least about 6 carbon atoms, preferably at least about 8 carbon atoms, and usually not more than 16 carbon atoms, more usually not more than 12 carbon atoms. Conveniently, the 2-ethylhexanoates have found use, although neodecanoates, or other branched chain, particularly alpha-branched chain fatty acids

may be employed. The metal soaps are prepared in accordance with conventional procedures. The soaps are dispersed in an appropriate medium, particularly hydrocarbons or halohydrocarbons boiling in the range of about 40°C to 100°C, such as chloroform, toluene, xylene, benzene, methylenedichloride, etc., and the mixture made homogeneous by agitation, for example shaking, for several hours. Adjuvants may be added, such as thickeners, e.g. polysaccharides or ultra-high molecular weight polymers. The resulting solution and/or dispersion is then coated onto the substrate.

Coating can be achieved by putting the viscous sol onto the surface to be coated and spinning the surface by centrifugation for a short time to ensure the substantially uniform distribution of the film. Alternatively, the substrate may be dipped into or sprayed with the dispersion, protecting those areas of the substrate which are not to be coated. Any technique which allows for substantially uniform coating of the film on the substrate may be employed.

The coated substrate is then pyrolyzed for a short time at an elevated temperature, generally in the range of about 150°C to 500°C, preferably in the range of about 150°C to 300°C. Tl volatilization can occur at temperatures as low as 100°C, so that short process timing and Tl overpressures and oxidizing atmospheres are employed to control phase formation and to limit Tl loss and formation of undesired second phases in the film. The pyrolysis time and temperature should be selected to substantially ensure decomposition of the fatty acids, so as to leave a thin film of metal oxides, the pyrolysis occurring in the presence of oxygen, conveniently air. The procedure may be repeated as many times as desired, in order to enhance the thickness of the metal oxide film.

Desirably, each subsequent pyrolysis may be carried out at a lower temperature than the initial pyrolysis, where the initial pyrolysis is carried out in the upper portion of the temperature range, 250-450°C, and the subsequent pyrolyses are carried out at a temperature in the range of about 200-350°C. Usually, at least about 60% of the volatile organic material is removed and by extending the heating period, a constant weight can be realized. Care must be taken to minimize thallium volatilization when pyrolysing above 300°C.

The film, deposition and pyrolysis procedure will be carried out at least once, more usually twice, and may be five times or more, usually not more than about four times.

The thickness of each layer will depend upon a number of parameters: the viscosity of the sol, the time for spinning, the revolutions per minute, the temperature at which the substrate is spun, and the like. Where other techniques are used to provide the coating, such as dipping, spraying, spreading with a blade, or the like, different parameters may be involved.

Once the substrate surface has been coated to the desired degree, the substrate may then be introduced into a closed inert vessel, containing pellets with the appropriate molar ratio for maintain-

ing the stoichiometry of the film in the presence of a source of oxygen during heating. The molar ratio of the pellets is determined by the phase that is desired within the film. The film composition after heating is substantially affected by the geometry and temperature of the source material and the resulting Tl overpressure.

Maintenance of a controlled thallium overpressure may be achieved in a variety of ways. The simplest way may be to coat the layer containing the mixture of oxides with a thallium oxide layer, so that vaporization of the thallium oxide overcoat provides for thallium overpressure. To ensure sufficient thallium for incorporation in the superconductor layer, the housing for the thermal treatment of the superconductor layer should desirably be relatively small, so that a relatively small volume is occupied by the vapor. By relatively small is intended a volume of about 0.001 to 10 times the size of the substrate. In addition, compared to the surface of the superconductor layer, the surface of the thallium source should be relatively large, at least about one and a half times, preferably about two times, and maybe five times or more. In addition, the thallium oxide is desirably combined with calcium oxide and copper oxide, where the composition may be varied, depending upon whether the source is present during crystal growth or for stabilizing the thallium superconductor material after it is in the correct phase.

Conveniently, in the gas phase, air, pure oxygen, or other source of oxidizing oxygen may be employed, e.g., hydrogen peroxide or ozone during heating. The pellet composition will vary depending upon the particular thallium superconductor one wishes to prepare. For example, for the 2223 composition, the pellets will have a Tl: Ca: Ba: Cu 1:3:1:3 molar ratio. The inert tube is conveniently a passivated noble metal, most conveniently gold or plated quartz, which may be externally reinforced to support the pressures during the reactions.

The processing temperature will be at least about 600°C, more usually at least about 630°C, and not more than about 950°C, frequently in the range of about 800-900°C. The temperature may be monitored in any convenient way, conveniently a thermocouple. Usually, the temperature will be achieved rapidly, generally under five minutes, preferably under three minutes, more usually from about 0.5-3 minutes. Slower heating rates (20°C/min) may be employed to give continuous superconducting films of smaller grain size. The tube may be heated to a temperature or temperatures in the range indicated above, generally for sufficient time to ensure complete pyrolysis of any residual carbon compounds and allow for the atoms to assume the proper lattice structure. Generally, the time at high temperature will be at least about 0.5 minute and not more than about 60 minutes, more usually in the range from about 0.5 to 25 minutes, preferably from about 0.5 to ten minutes. At the end of this time, the tube may be removed from the heating source and allowed to cool. Normally, there need not be any effort at rapid quenching, so that the tube may be allowed to sit in a room temperature environment, without providing for a rapid reduction in temperature.

A second preferred procedure for preparing the subject films employs laser ablation. Laser ablation can be used either to coat the substrate at room temperature in preparation for the thermal process described above, or can be used to deposit and form the superconducting phase in one step at elevated temperature.

In accordance with this invention, laser ablation is achieved by preparing an appropriate target. The apparatus for the most part, is conventional and is described in Wu et al, supra. A target is prepared by placing the appropriate composition of metals or metal oxides on the surface of a support which can be rotated at a controlled rate. The target on its support is placed in a vacuum chamber having a quartz window, where a laser beam of appropriate energy and wavelength impinges on the target causing a plume of ablated vapor normal to the target surface. The substrate is placed substantially normal to the direction of the plume, so as to receive the atoms in the plume, where the atoms bind to the surface of the substrate. The substrate is maintained at room temperature or at an elevated temperature depending on whether the goal is an amorphous or a crystalline deposit.

The laser ablation target can conveniently be made in the same manner as the sol-gel coating described earlier. Thus, a uniform film of the various carboxylates can be prepared and pyrolyzed as described previously to produce the desired oxide mixture. Pyrolysis can be carried out in the presence of oxygen, so as to ensure the formation of the desired metal oxides in their proper oxidation state. Alternatively, the target can be made from pressed and sintered powder or from hot pressed powder.

The laser energy density on the target will generally be from about 1-3 J/cm². The film on the target will have the same metal molar ratio as the intended composition on the substrate. The target will usually be of from about 0.5 to 10 in.² in surface area and about 0.001 to 0.25 in. thickness.

The laser may be focused to cover various areas of the target. The laser may impinge upon the surface over a wide range of angles from a minimum of about 2° up to 90°. A typical impingement angle is about 25°. The area impinged by the laser will generally be at least about 2mm² and not more than about 50mm². A typical area is about 15mm². The ratio of length to width will depend upon the angle of impingement, and will generally be at least 2 to 1, and not more than about 20 to 1, more usually not more than about 10 to 1. By employing an energy in the range of about 2 J/cm² per pulse, one can deposit about one monolayer, generally about 3A° thick onto the substrate with each pulse. By controlling the number of pulses per second, which would generally range from about 0.5 to 50, one can achieve an accretion on the substrate of about 0.1μm/min.

The target will usually be relatively close to the substrate, usually not less than about 2cm and not more than about 10 cm, preferably about 6 cm. The chamber will be evacuated to under about 500mTorr, preferably from about 2 to 200mTorr, more prefer-

ably about 100 to 200mTorr. Various inorganic oxidizing gases may be present, such as oxygen, air, hydrogen peroxide, ozone, nitrogen oxides, such as nitrous oxide or the like, where the inorganic oxygen source can be activated by virtue of the laser beam or an independent energy source. For example, an oxidizing gas source may be directed toward the layer on the substrate where the gas has been activated, for example, oxygen activated by passing through an electric field or laser.

For growth of crystalline superconducting films the substrate will generally be maintained at a temperature in the range of about 450-750°C, preferably about 500-650°C. The temperatures which are maintained will allow for the atoms to form the proper crystal structure, but should be kept as low as possible to minimize interdiffusion between the film and substrate and to minimize thallium loss by vaporization. The lower the temperature which is used for the substrate, the slower the deposition rate which should be employed. Alternatively, one can increase the energy of the atoms and molecules in the plume by providing for a plasma in the ablated plume. This additional energy increases the atoms' ability to form the proper crystal structure at low temperature, and increases the rate at which the film may be grown.

In some instances, where thallium may be lost because of its higher vapor pressure, it may be desirable to increase the amount of thallium in the target. Alternatively, thallium loss can be minimized by maintaining a higher oxidation potential in the apparatus.

It may be desirable to sequentially ablate one or a combination of metals or metal oxides, so that layers of different composition are deposited sequentially to provide the different atomic layers of the crystal.

Besides deposition on elevated temperature substrates as described above, laser ablation can be used to deposit onto room temperature substrates prior to thermal processing. Laser ablated films on room temperature substrates are dense, uniform and high purity, but are not crystalline. These amorphous films, when heated, form liquid and then solid crystalline phases in the manner previously described for chemical processing. The kinetics of liquid phase formation is somewhat different for the two kinds of films because the chemically prepared films tend to be highly porous, and may contain some residual carbon before thermal processing.

The processes may be further modified by employing layers of different composition. Of particular interest is having an initial layer of thallium oxide, preferably a combination of thallium oxide and calcium oxide, with a second layer comprising at least copper and barium oxides, desirably comprising thallium and calcium oxides as well. These layers can be achieved as described above, using the various processes which allow for the independent application of different compositions as layers on the substrate. For example, with the sol-gel technique, one could first provide for a layer of thallium and calcium carboxylates, which may or may not be pyrolysed prior to coating with a layer of carboxylates of all of the metals.

An alternative procedure for coating the substrate, may employ the physical method of tilting. By employing a boat which can be tilted, so that the liquid composition can be kept away from the substrate, a liquid of the various oxides may be produced. Once the liquid is formed, the boat may be tilted, so that the liquid now coats the substrate, which is in the other part of the boat. Desirably, the substrate may be positioned, so it is at an angle to the bottom of the boat, with the higher end near the wall of the boat. The conditions under which the coating is carried out would provide for a rapid rise to a temperature in the range of about 500 to 880°C, at which point the oxides would be in the liquid form. The boat can then be tilted and cooling begun at a relatively slow rate, in the range of about 0.5-10°C/min until the temperature has dropped at least about 10°C, preferably not more than about 50°C, when the temperature is in the range of about 490-860°C. At this point, the boat would be tilted back to the original position, where the substrate was no longer in the liquid, and the substrate would be rapidly cooled at a rate of at least about 10°C/min, preferably at least about 20°C/min to room temperature.

Various configurations may be employed during thermal processing between the source and the superconductor film. The source should not be allowed to contact the superconductor film. The configurations may allow for the source being in a confronting relationship to the superconductor film. For example, a substrate coated with the source may be spaced from the substrate coated with the superconductor film by a spacer (typically 5 microns or greater in thickness), where the source and film are in a confronting relationship.

An alternative configuration would have the superconducting film on a substrate in a container, where the source is displaced from the superconductor film and is maintained at a temperature differential from the superconductor film. Thus, by varying the temperature of the source, different thallium overpressures would be achieved, so as to ensure the proper Tl stoichiometry at the superconductor film surface.

Various regimens may be employed for producing these superconducting films and for use in a postannealing of the superconducting material. By employing schedules for heating and pressure that inhibit the evaporation or boiling of the liquid in the film prior to formation (precipitation) of the superconducting material, one can provide for condensation of Tl source material, so as to provide for precipitation of the superconducting phase, and can minimize or prevent the formation of nonsuperconducting oxide compositions.

One protocol would initially provide for a pressure of about 3 atm with a rapid rise in temperature from room temperature to 850°C, at about 50°C/sec rise, so that the temperature is reached in about 15 to 20 sec, maintaining the superconducting film at this temperature, where approximately 100 sec will have elapsed from the initiation of heating, allowing the superconductor to cool over a period of about 5 to 10 sec to a temperature of about 550°C and

maintaining the temperature for an additional 100 sec, followed by cooling to room temperature. During this time, a different heating profile is employed for the source material, where the source is heated at about the same rate along with the superconductor film, but is maintained at the high temperature for about 5 to 25 sec longer than the superconducting film, so that the overpressure is maintained relatively constant while the superconducting film is undergoing its initial cooling, followed by dropping the source temperature by about 100°C and maintaining this temperature during the annealing of the superconducting layer. The temperature is then allowed to drop to room temperature along with the superconductor layer. The pressure profile would be to maintain the elevated pressure until the annealing temperature has been reached and then allow the pressure to drop to 1 atm.

Where the source and superconducting layer are both maintained at the same temperature, a different protocol would provide for heating at about 40 to 70°C/min to 800°C, where the temperature is achieved in from about 15 to 40 sec, preferably about 20 to 30 sec, while maintaining an oxygen pressure at 3 atm. The elevated temperature is maintained for an additional 60 sec and then reduced at a temperature drop from about 5 to 20°C/sec to room temperature. The pressure profile differs in being maintained at the elevated pressure for about 60 sec, and then allowed to drop to 1 atm over about 10 to 20 sec. By adjusting the liquid composition, growth may be achieved at one atm pressure.

Parameters for a thermal anneal will vary from the preparation of the superconducting film. For the anneal, the superconducting film is rapidly heated to a temperature in the range of about 500 to 750°C, generally over a period of about 10 to 30 sec. The temperature will then be maintained, ± 15% for a period of about 5 to 60 min, preferably from about 15 to 45 min in an oxygen atmosphere while in the presence of a thallium source. The temperature for the source will be higher by at least about 50°C, preferably from about 100 to 150°C higher than the superconducting film. The temperature of the source will be heated analogously to the superconducting film, so that the ultimate temperature for the source is reached at or shortly after the temperature for the film is reached. The temperature for the source will be maintained substantially constant during the period of annealing and will then be allowed to cool at about the same time as the superconducting film back to room temperature, as well as at about the same rate. Desirably, cooling of the source will begin shortly before the cooling of the superconducting film, usually from about 0.5 to 5 min prior. During the annealing, an elevated pressure may be employed, usually about 1.5 to about 2.5 atm, preferably up to about 2 atm.

Localized effects can be achieved by employing infrared heating. For example, the substrate with the pre-superconductor or precursor film could be placed in an enclosure having an infrared transparent window above the film and having a small volume relative to the substrate. By employing infrared heat, vaporization would occur in a small volume with a rapid increase in pressure. Furthermore, the assembly could be introduced into a pressure vessel, which would also have an infrared transparent window, so that the entire assembly could be pressurized. In this way, the gas environment in which the superconductor film is formed would be rapidly saturated with thallium oxide vapor. The process may be carried out at atmospheric or superatmospheric pressure.

By placing the substrate on a large thermal mass base, and using infrared heating, a heat flux will occur at the substrate precursor film interface, since the substrate will have higher thermal conductivity than the precursor or the intermediate liquid composition. Thus, there will be a temperature gradient in the film and substrate, where the precursor film will be at a higher temperature than the substrate. The cooler substrate can then provide a site of nucleation for the formation of the superconductor film.

For further understanding of the invention, the drawings will now be considered. In Figures 1 and 2 are depicted different views of tubular devices and arrangements for production of superconductor films. The gold sealed vessel 10 houses thallium pellet sources 12 and 14. A substrate 16 separates pellet 12 from the superconductor layer precursor 20. A wire horseshoe spacer 22 prevents the pellet source 14 from touching the superconductor layer 20. Prior to sealing tube 10, the various components may be assembled to provide the indicated assembly and introduced into the housing 10. The housing may then be sealed and intro duced into a furnace where it is rapidly heated to the desired temperature and maintained at that temperature. However, it is not necessary to seal the pouch in order to prepare high quality films using this process geometry. Usually, a small amount of air or oxygen will be allowed to remain in the sealed housing 10. Upon heating, the pellet sources will partially evaporate, so as to maintain a thallium oxide overpressure in the housing 10, to prevent significant evaporation of thallium oxide from the superconductor precursor layer. After sufficient time for the superconductor layer to form, the tube may be allowed to cool by turning off the furnace and letting the furnace chamber come to room temperature.

In Figure 3, an alternative embodiment is provided, where infrared heat is employed to produce the desired temperature. Mounted on a base 30 is cover 32 having conduit 34 and valve 36 for evacuating or pressurizing the chamber 40. The cover 32 has an infrared transparent ceiling 42 to allow for transmission of infrared rays into chamber 40. An infrared source 44 is provided which is able to irradiate the entire chamber. A removable mask 46 is provided which when in place prevents radiation from heating the superconductor film precursor 50. The superconductor film precursor 50 is coated onto substrate 52 which sits on base 30. A thallium oxide ring 54 is mounted on support 56 inside the chamber, where the thallium ring will be exposed to the infrared radiation when the mask is in its position.

In preparing a superconductor film, one would place the substrate 52 coated with the superconductor precursor film 50 onto the base 30 and then

mount the cover 32 on the base. The chamber may then be filled with oxygen and irradiation with the infrared lamp 44 begun, with the mask in place. When a sufficient thallium oxide partial pressure has been achieved, the mask may be removed and the precursor film 50 heated to an elevated temperature, so as to provide for formation of the superconductor film. After sufficient heating, the lamp 44 may be turned off, the chamber 40 allowed to cool to room temperature, evacuated, and the cover removed for isolation of the superconductor film.

In Figure 4, an alternative embodiment is indicated, where one or more substrates may be coated with a superconductor film precursor, where the substrate may be repetitively coated, until a layer of the desired thickness has been achieved. A housing 60 is provided having conduit 62 with pressure gauge 64 and valve 66. The base of the housing 60 has two heaters, 70 and 72 which can provide heat to vessels 74 and 76 respectively. Attached to one end of vessel 74 is rod 80 which extends through orifice 82 outside of housing 60. Seal 84 prevents the introduction of air or loss of vapors into housing 60. Substrate 86 is situated in vessel 74 supported at an angle by mount 90. By means of rod 80, vessel 74 may be moved from position A, where the surface of the liquid precursor to the superconductor film is substantially parallel to the base 78 of housing 60. In this position, the substrate 86 is immersed in the superconductor precursor liquid. By lowering the temperature or evaporating some of the solvent, crystallization of a superconductor film on the substrate is induced. By raising the rod 80, or tilting the entire apparatus, one can then move the liquid to position 92 indicated by the broken lines B, so that the substrate 86 and superconductor film is no longer coated with the superconductor precursor liquid 94. Vessel 76 will contain thallium oxide liquid 96 which may serve to provide a thallium oxide overpressure in the housing 60. The temperature of the thallium oxide liquid 96 may be maintained at a lower temperature from the superconductor precursor liquid, since it will be solely comprised of thallium oxide, and can be used to control the overpressure in the housing 60.

The subject device components can be used in a wide variety of devices. Because superconductive layers have low microwave surface impedance, they find use in numerous microwave and millimeter wave applications. The subject elements comprising the substrate and film, by appropriate choice of substrates, may find use in radio frequency cavities and resonators, microwave shielding, antennas, in transmission lines, employing different structures, such as coaxial, microstrip, coplanar wave guide, coplanar strip line, inverted or suspended microstrip, and the like. The devices find use in signal communications or delays, filters, resonators and oscillators, circuit interconnections, power combiners, and antenna feeds.

For a narrowband microwave filter with superconducting resonator elements, the specifications could be:

Transmission medium: microstrip coupled lines (5-15 resonator elements)

Bandwidth: 0.1-10% at the center frequency (f_o)
Dimensions:
Superconductor thickness (t) = 1 micron Relative dielectric constant
(ε_r) = 9.65 (MgO)
Loss tangent = .0002 (MgO)
Substrate height (h) = 25 mils
Spacing (s) = 10-150 mils
Line width (w) = 1-40 mils Length (1), 0.25 guide wavelength at f_o,
1 = 114 mils at $10GH_z$
Package dimensions:
X = 1 in.
Y-1 in.
Z = .25 in.

The filter is packaged in a shielded case and cooled to 77°K and connected with an SMA coaxial connector to other hardware part.

An exemplary narrow band microwave filter with superconducting resonator elements is depicted in Figure 5. The filter comprises antenna 100 which feeds the signal to microwave filter 102. The signal from microwave filter 102 is fed to mixer 104 in conjunction with signal 106. A swept local oscillator 110 also feeds a signal into the mixer 104, which provides an output to dispersive delay line 112 in conjunction with signal 114. The superconducting resonator elements 116 are shown in an array where "w" is line width, "s" is spacing and "1" is length. The low loss of the narrow band microwave filter enables the microwave receiver to have a relatively higher signal to noise ratio. The dispersive delay line is used to process long pulses (higher energy) as if they were short pulses (higher range resolution). First described by R.H. Dicke, U.S. Patent No. 2,624,876, issued January 6, 1953.

Delay lines are an integral part of a digital instantaneous frequency measurement (DIFM) component. The delay line specifications could be as follows:
Dimensions:
Superconductor thickness (t) = 0.015 μm -2 μm
ε_r = 9.65 (MgO)
Loss tangent = 0.0002 (MgO)
Substrate height (h) = 25 mils
Line width (w) = 0.04-40 mils
Total length (1) = 20 mm
Package dimensions:
X = 1 in.
Y = 1 in.
Z = .25 in.

The delay line can be packaged in a shielded case thermally attached to a 77°K cold finger with SMA coaxial connectors interconnecting the delay line within the DIFM.

A digital instantaneous frequency measurement is diagrammatically depicted in Figure 6. The antenna 120 feeds a signal to a diode 122 which feeds the signal to power splitter 124. The power splitter 124 outputs directly to phase detector 126 through lines 130 and 132 which comprises delay line 134 comprised of the superconductor film. The outputs of lines 130 and 132 are fed into phase detector 126, which then outputs signals 136 and 140 to video 142.

The following examples are offered by way of

illustration and not by way of limitation.

EXPERIMENTAL

The individual Tl, Ca, Ba and Cu metal carboxylate compounds were prepared following established procedures. The resulting solutions of metal soap compounds in chloroform were reduced in volume by evaporation and analyzed by atomic absorption for their metal contents. These precursor solutions were then used to prepare the precursor sol by combining 5g copper 2-ethylhexanoate, 3.29g barium 2-ethylhexanoate, 3.14g calcium 2-ethylhexanoate, and 8.462g thallium 2-ethylhexanoate in 5 ml of chloroform. The precursor stoichiometry was $Tl_2Ca_2Ba_2Cu_3$. The solution was mixed by shaking for several hours. This precursor solution was spun onto a single crystal yttria-stabilized zirconia (<100> orientation) substrate at 4000 rpm for 30 sec followed by pyrolysis at 400°C for 5 min. This spin/pyrolysis procedure was repeated twice more at 250°C. Oxide pellets with a molar ratio Tl:Ca:Ba:Cu-1:3:1:3 were prepared by mixing the individual oxides together by grinding and then pressing uniaxially in a Carver press. The pellets and the coated substrate were placed in air in a $1/4$" diameter gold tube and hermetically sealed. The sealed gold tube was attached to a thermocouple probe using wire and inserted into a preheated tube furnace. The material was brought to a temperature of 855°C in 2 min and held for 10 min. The sample was then removed from the furnace and cooled to room temperature. The entire film processing procedure required about 15 min to complete.

Optical micrographs of the pyrolyzed film revealed the presence of a large number of plate and needle-like (plate on edge) structures throughout the film. Both structures were found to have, by energy dispersive x-ray analysis, the 2223 composition. Scanning election microscopy of the film showed the plate-like morphology of the superconducting 2223 compound. The micrograph also showed the spherical Ca/Tl oxide deposits that inhabit regions immediately adjacent to the plate-like structures. The composition of the plate was determined by SEM-EDX (scanning electron microscopy energy dispersion x-ray spectroscopy) to consist of 12 atomic percent Ba, 12 Tl, 12 Ca and 20 Cu. The compositional analysis results were consistent from area to area and are consistent with the material possessing a 2223 metal stoichiometry. The highly oriented nature of the 2223 film is indicated by the large enhancement of the <001> reflections in an x-ray diffraction scan. A minor peak at 6° was indicative of a very small amount of the 2122 phase in the film. The temperature dependent magnetic susceptibility measurement was performed on the film on the assumption that the material consisted of a 2 micron thick fully dense film. It was calculated that greater than 60% of the material became superconductive.

To prepare the 2122 composition, the above procedure was repeated, except the composition of the source material corresponded to a Tl:Ca:Ba:Cu atomic ratio of 2:2:2:3. The temperature was slightly modified to 860°C for reaction and the substrate which was employed was a magnesium oxide substrate single crystal that had been chemically polished using hot concentrated phosphoric acid as described previously (See Sanywal and Sutaria, J. Mater. Sci. (1976) 11:2271-2282) to provide a substantially defect free (<100>) surface.

Optical micrographs of the pyrolyzed film revealed the presence of a large number of plate-like structures throughout the film. These structures were found by SEM-EDX to have a chemical composition corresponding to the 2122 material. SEM of the film clearly showed the plate-like morphology of the superconducting 2122 compound. The film was highly c-oriented as indicated by highly enhanced <001> reflections. The film was found to be epitaxial by comparing electron channeling patterns of the single crystal substrate with that of the film in various regions. The morphology of the film is strongly indicative of the presence of an intermediate liquid phase during processing. The surface of the film (which resembles thin film surfaces obtained by liquid phase epitaxial growth techniques), was analyzed by EDX to have the correct cation stoichiometry for the 2122 compound.

Electron beam channeling patterns were obtained from many representative areas within the film. Electron channeling patterns of the film revealed that the orientation of the a, b plane within the 2122 film was identical to that of the substrate in many areas throughout the film. In a few areas, the channeling pattern of the film was slightly misoriented (by a constant amount) from the substrate, perhaps indicative of a buildup of strain or dislocations at the film/substrate interface due to lattice mismatch which is approximately 9%. The lattice registry with the surface was maintained not only at layers close to the magnesium oxide substrate, but also at top of plates many microns from the substrate surface.

To deposit a thallium-based superconducting film by PVD, for example of the 2223 composition, a substrate is loaded into a specially designed vacuum chamber, and held in position where it faces a target approximately 6 cm away. The vacuum chamber is evacuated to a pressure of less than 1 x 10⁻⁶ torr, then back filled to 5 x 10⁻³ torr with oxygen, while the substrate is heated to a temperature between room temperature and 400°C. Material is then vapor transported from the target to the substrate by laser ablation, using a laser energy density on the target of 1.5 to 2.0 Joules/cm². The laser is pulsed at 5Hz for 5 to 10 minutes, depositing a film 0.5 to 1.0 μm thick. After ablation, the film is cooled to room temperature and the substrate removed from the vacuum chamber.

The film thus deposited is continuous and smooth over the entire substrate. In some locations there are particles on the film surface that appear to have been transported from the target either in solid particle form or as small melted globules. The film composition, measured by energy dispersive x-ray (EDX) spectroscopy, is found to be the same as the target composition for substrate temperatures up to

400°C. Thus if the target has the 2223 composition, the film has the same composition. When the substrate temperature is 600°C, the maximum content of the film is lower than that of the substrate because the film loses thallium by evaporation. The loss can be compensated by increasing the thallium content of the target.

The films are not superconducting as deposited, but become superconducting after annealing at 750-850°C in a gold pouch containing a source of thallium vapor.

An additional number of preparations were carried out using a variety of substrates. The substrates include polycrystalline forms of magnesium oxide, zirconia and alumina, as well as single crystal sapphire. The films are prepared by coating a chloroform solution of Tl, Ca, Ba and Cu 2-ethylhexanoates onto the substrate and pyrolyzing the film at 250°C. This process is repeated up to as many as 10 or more times to develop the desired thickness prior to high temperature processing. A film thickness of 5μ is obtained after coating a substrate three times.

The chemically deposited films are prepared by first coating cleaned substrates three times as described above. The prepyrolyzed film is amorphous by XRD and TEM. The film consists of an intimate mixture of the metal ions, where the Tl, Ca stoichiometry of the film prior to high temperature pyrolysis has not been found to be particularly critical to producing the high temperature superconductor (HTSC) material. However, if excess Ba and Cu are added, large hexagonal crystals of barium cuprate are produced during high temperature pyrolysis.

High temperature thermal processing is carried out using the following procedure. The initially amorphous chemically deposited film is placed between two source pellets. The source materials are typically 1/2 inch diameter uniaxially pressed powder compacts of Tl-Ca-Ba-Cu oxides. The stoichiometry of the source material plays a critical role in determining the phase(s) that are produced during processing. The two most common source compositions that are used are Tl-Ca-Ba- Cu ratios of 1313 and 2223. A spacer is placed between the pellets and a film inserted between them. The film surface is prevented from touching the surface of the pellet through the use of a ceramic or metal spacer. It is important to prevent contact of the film with the source material in order to obtain morphologically uniform films over large areas (> 1cm²). Contact of the film with the source material often destroys the uniformity and integrity of the final fired film.

The source/film structure is inserted into a preconditioned gold tube. The gold tube is then purged with air, nitrogen or oxygen, and closed (hermetic seal is not necessary). The material is then heated to a final temperature ranging between 600° and 910°C. The heating rate that is employed is important. Slow heating rates ranging from 10-30°C/min usually produce polycrystalline, unoriented films that range in thickness from 2-10 microns. Faster heating rates produce oriented films. The typical range of heating rates used to produce oriented films is between 50-500°C/min. The higher heating rates are obtained by placing the gold pouch directly into a preheated tube furnace and monitoring its temperature by using a thermocouple inserted directly into the pouch. The film orientation that is obtained upon rapid heating of chemically deposited films is largely the c-axis of the material normal to the substrate surface. Rocking curves as sharp as 0.3 degrees have been obtained for such materials. Some evidence for nucleation of material with its C-axis parallel to the substrate has also been observed; however this material represents a small volume fraction of any particular film. Epitaxy has been demonstrated for single crystal MgO substrates.

The degree of orientation of the film is intimately related to the phase formation process. The intermediate liquid phase that is obtained during high temperature processing plays a key role in controlling the morphology, phase identity and purity, crystallographic orientation and density of the film. The studies show that the intermediate liquid phase obtained consists primarily of Tl and Ca oxide at low temperature (ca., 600°C). Large grains of the 2-layer material have been observed at temperatures as low as 650°C for rapidly heated samples, indicating that liquid phase formation is indeed occurring at these relatively low temperatures. DSC experiments on pyrolyzed chemical precursors corroborate these findings. Slow heating rates (i.e., 10°C/min) result in a relatively small amount of liquid phase (per unit volume) being produced in the film and a large number of nucleation sites within the film. These factors combine to produce fine grained material (<5 microns) exhibiting a very low degree of crystallographic orientation. The nucleation is random in orientation and occurs throughout the deposit, resulting in a randomly interconnected platelet structure of the superconducting material. The coverage of the film on the substrate is excellent and uniform - apart from the fact that the film is a fairly porous network of 5 micron grains of material. A surface resistance measurement of a polycrystalline film on single crystal MgO revealed that the material had a reasonably low loss with a surface impedance that was approximately a factor of two greater than cryogenic copper at 50K and 10 GHz.

On the other hand, rapid heating rates (> 50°C/min) produce a markedly different film morphology. During rapid heating of the precursor film, a large volume fraction of liquid phase is produced. The liquid, which initially consists primarily of Tl and Ca oxides, rapidly dissolves any barium and copper in contact with it and directly precipitates out the 2122 or 2223 compound. The liquid phase is very mobile and formed early in the heating process. Material transport via this intermediate liquid phase is extremely rapid. Thus an initially porous 5 micron (low initial. density) thick film can shrink in thickness to just over 1 micron during processing. The phase that is produced from the liquid depends upon the overpressure that is in equilibrium with the liquid. The use of source materials that contain the 2223 phase (or produce it during the anneal experiment) will typically result in

films that contain the 2223 phase. The local thallium overpressure is important to determining the phase that is produced from the liquid. If the overpressure is too low, no superconducting material is obtained.

The degree of crystallographic orientation of the film can be readily controlled through appropriate selection of the film process condition. By employing heating rates between 20 and 50°C/min (the end regimes for polycrystalline and oriented/epitaxial film growth), partially oriented films exhibiting a range of morphologies, densities, and thicknesses can be obtained.

Sharp superconducting transitions have been obtained for 2 layer films both by resistivity measurements (R=O at 107K) and AC susceptibility. An oriented 2122 film produced by this process on single crystal MgO has apparently the lowest surface resistance at 77K of any HTC film or bulk material that has been reported. This material was oriented and, perhaps, epitaxially related to the substrate. Films prepared using the same processing parameters were found to exhibit very sharp x-ray rocking curves; typically less than 0.7 degree full width at half maximum (FWHM). Values as low as 0.3 degrees were also obtained. This value is comparable to the best rocking curve data that have been reported for HTSC thin films of any material. Additionally, further improvement may be achieved with optimization of this process.

For rapid thermal annealing of films with a Tl overcoat, the following experiment was performed. A coating of Tl 2-ethylhexanoate was spun onto a prefixed film containing the oxides of Ca, Ba and Cu. The initial film was prepared by firing a normal stoichiometry film (2223) in a Tl overpressure insufficient to prevent complete vaporization of Tl from the sample. A total of three Tl overcoats were added followed by firing in an oxygen atmosphere at 860°C in a sealed gold pouch. A source pellet was included in the pouch to control the Tl overpressure. After processing, the film contained a large amount of 3-layer superconducting material.

In the next experiment, a 2223 mixture of the appropriate metal cations was dissolved in nitric acid and the solution evaporated onto a single crystal MgO substrate. This material was dried in a box furnace at 80°C and fired in a gold pouch using the normal procedure. The 2122 compound was formed from the thermally processed nitrate precursor. The morphology and composition of a number of areas of the film (SEM-EDX) were entirely consistent with the presence of the 2122 material. Other solutions or colloidal dispersions that may be used to deposit precursor films include carbonates, citrates, hydroxides, fluorides, chlorides, and acetates of these metal ions. Tl, Ca, Ba or Cu salts can share the same counterion (i.e., all be chloride salts), or consist of various complex mixtures of different anions. The precursors are fired under the appropriate conditions to complete phase formation and removal of the counterions (i.e., removal of halides requires heating under a water-containing atmosphere, oxygen atmosphere for organics).

Studies have conclusively shown that the intermediate liquid phase that was used to engineer the morphology and properties of the films can be very reactive with a number of different materials of technological interest. Direct physical contact of the partial melt produced within the film can result in degradation of the superconducting material; particularly on substrates such as sapphire or polycrystalline alumina. Often after processing the films on Al-containing substrates the presence of barium-aluminate crystallites in the film has been observed. The obvious corrosion of single crystal plates of the 2122 or 2223 compound that were produced early on during thermal processing but were subsequently dissolved by contact with liquid during processing to degrade the material were noted.

Superconducting Tl films on sapphire substrates are produced without interference from the substrate by employing the following technique. The first is to fire the film using an intermediate heating rate (approximately 50°C/min) that effectively serves to limit the amount of liquid phase that is present at any particular time during the process. The second is to limit the substrate reaction by reducing the amount of time the material is at high temperature. Both of these techniques have been demonstrated in the laboratory to be successful for controlling deleterious substrate reactions of the 2122 or 2223 phases on sapphire substrates.

Other than lowering the temperature or shortening the time at temperature, another method for reducing substrate reaction is to deposit a barrier layer onto the troublesome substrate material. MgO and Y-stabilized zirconia as buffer layer materials on sapphire, silicon and gallium arsenide substrates may be employed. Zirconia (yttria stabilized) and magnesium oxide demonstrated phase compatibility with these materials under the subject current process conditions. The buffer layer material can either be epitaxial or polycrystalline.

A number of preparations were carried out using the following experimental procedure.

The metal 2-ethylhexanoate precursor solutions were prepared using standard published synthetic procedures. The film itself was generated by spinning a solution prepared from copper 2-ethylhexanoate, barium 2-ethyl hexanoate, calcium 2-ethylhexanoate and thallium 2-ethylhexanoate onto the appropriate substrate. The film thickness was adjusted by controlling solution viscosity, spin speed, spin time and number of coats. Typically the substrate was spun at 3000 rpm for 30 sec. After each precursor coat, the film was fired at 250°C for 6 min to pyrolyse the 2-ethylhexanoate. This was repeated three times to build up sufficient thickness of the precursor material.

The pyrolysed films were loaded into gold pouches containing oxide pellets of known stoichiometry (for example Tl/1: Ca/3: Ba/1: Cu/3) and compression sealed. Both air and oxygen atmospheres have successfully produced the superconducting phase. The charged gold capsule was heated in a horizontal tube furnace at a temperature ranging from 750°C to 920°C and for times from 30 sec to 5 min and in all cases the superconducting phase was identified by powder X-ray diffraction and energy dispersive X-ray analysis. A typical ex-

perimental procedure is outlined below:

5g copper 2-ethylhexanoate, 3.29g barium 2-ethylhexanoate, 3.14g calcium 2-ethylhexanoate and 8.462g thallium 2-ethylhexanoate in a minimum volume of chloroform were mixed by shaking for several hours. This precursor solution was spun onto a 1x1cm single crystal yttria-stabilized zirconia (>100< orientation) substrate at 3000 rpm for 30 sec followed by pyrolysis at 250°C for 6 min in a Lindberg box furnace. This spin/pyrolysis procedure was repeated twice more at 250°C. The coated substrate and oxide pellets with molar ratio Tl:Ca:Ba:Cu 1:3:1:3 were loaded into the gold pouch under air. The film was sandwiched between two pellets and the film surface kept from the pellet itself using a spacer made from thermocouple wire. This whole package was heated in a Lindberg 1" tube furnace from 25°C to a temperature of 855°C in 10 min and held for 4 min. Cooling to room temperature took a further 5 min and was achieved by opening the furnace.

Advantages of the laser ablation method include the cleanliness inherent in vacuum deposition, precise and repeatable control of the rate of film growth, control of film stoichiometry via the target composition, control of oxygen activity via the choice of oxygen species and/or plasma activation, and the ability to grow on a substrate at elevated temperature to encourage epitaxial growth.

The subject articles comprising superconductive thallium-based layers on crystalline substrates provide for an extraordinary advance over previously prepared materials. The subject articles have superconductive properties at liquid nitrogen or higher temperatures, are highly oriented and in many instances are grown epitaxially on a crystalline substrate and as shown, provide for a number of highly desirable physical and electrical properties.

In addition, novel methods have been provided for producing the subject compositions, where growth can be carefully controlled, so as to provide for highly oriented and epitaxial films. In addition, the thickness can be controlled, so as to provide for greater homogeneity and uniformity of the sol-gel film. Also, the rate of growth of the crystallites is controlled under controlled temperature conditions, to provide for substantial homogeneity.

Advantages of the sol-gel technique include the capability to coat large areas uniformly, atomic-scale mixing of the components at room temperature, low temperature synthesis of mixed metal oxides, amenability to powder, bulk, film or fiber development, as well as attaining of high chemical purities.

The laser ablation system has the advantages of safety, the system is opened at room temperature, the opportunity to prepare the superconducting Tl films in situ, and the ablation and condensation zone may be surrounded by disposable shields, where stray thallium will deposit, rate of growth and thickness can be carefully controlled, and epitaxial growth can be encouraged.

The subject invention provides for a number of protocols for producing films of varying thicknesses having superconductive properties. The methods are convenient, allow for coating of a variety of substrates, and can provide different physical characteristics of the superconductive film.

All publications and patent applications cited in this specification are herein incorporated by reference as if each individual publication or patent application were specifically and individually indicated to be incorporated by reference.

Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

Claims

1. A superconducting article comprising an oriented superconducting layer of thallium, optionally calcium, barium, and copper oxide on a crystalline substrate, said layer being at least 30 Angstroms thick and having a c-axis oriented normal to the crystalline substrate surface.

2. A superconducting article according to Claim 1 wherein said superconducting layer is epitaxial to said substrate.

3. A superconducting article according to Claim 1, wherein said superconducting layer has the 2122 composition.

4. A superconducting article according to Claim 1, wherein said superconducting layer has the 2223 composition.

5. A superconducting article according to Claim 1, wherein said substrate is magnesium oxide or yttria stabilized zirconia.

6. A superconducting article comprising an superconducting epitaxial layer of thallium, barium, calcium and copper oxide on magnesium oxide.

7. A superconducting article according to Claim 6, wherein said superconducting layer is the 2122 composition.

8. A microwave or millimeter device comprising an article according to any of Claims 1, 6 and 7, wherein said superconducting layer is under about 1 micrometer in thickness.

9. A digital instantaneous frequency measurement device comprising:
a diode in signal receiving relationship from an antenna;
a power splitter;
a phase detector;
a delay line comprising an oriented superconducting layer of thallium, optionally calcium, barium, and copper oxide on a crystalline substrate, said layer being at least about 30 Angstroms thick and having a c-axis oriented normal to the crystalline substrate surface, said layer being in the form of an extended wire;
means connecting said diode to said power splitter and said power splitter to said phase detector; and
means for connecting said phase detector to an

output.

10. A microwave receiver comprising:
a microwave filter for receiving a signal from an antenna, said filter comprising an oriented superconducting layer of thallium, optionally calcium, barium, and copper oxide on a crystalline substrate, said layer being at least about 30 Angstroms thick and having a c-axis oriented normal to the crystalline substrate surface, wherein said layer is in the form of stepped strips coated onto said substrate;
a mixer;
a swept local oscillator;
a dispersive delay line;
means for connecting said microwave filter and swept local oscillator to said mixer and said mixer to said dispersive delay line; and
means for connecting said dispersive delay line to an output.

11. A method for producing a superconducting article comprising an oriented superconducting layer of thallium, optionally calcium, barium and copper oxide, said layer being at least 30 Å thick and having a c-axis oriented normal to the crystalline substrate surface, said method comprising:
coating a crystalline substrate surface with a liquid phase containing thallium, calcium, barium and copper oxides at an elevated temperature; and
cooling said solution, whereby said metal oxides crystallize on the surface to form a superconductive layer of said metal oxides as an oxide on said substrate.

12. A method for producing a superconducting article comprising an oriented superconducting layer of thallium, optionally calcium, barium and copper oxide, said layer being at least 30 Å thick and having a c-axis oriented normal to the crystalline substrate surface, said method comprising:
coating a crystalline substrate surface with a solution of thallium, calcium, barium and copper carboxylate soaps to produce a coating;
pyrolyzing said soap coating at an elevated temperature in the presence of oxygen and an overpressure of at least thallium oxide of said oxides in a predetermined ratio for sufficient time to produce a superconductive layer of said metals as an oxide on said substrate.

13. A method according to Claim 12, wherein said overpressure is supplied by pellets of at least thallium and calcium oxide mechanically removed from contact with said coating.

14. A method according to Claim 12, including the additional step of prepyrolyzing said soaps at a lower temperature than said pyrolyzing.

15. A method according to Claim 14 wherein said prepyrolyzing is at a temperature in the range of 250 to 450°C and said pyrolyzing is at a temperature in the range of 700 to 950°C.

16. A method according to Claim 12, wherein said substrate is magnesium oxide or yttria stabilized zirconia.

17. A method for forming a superconductive film consisting essentially of thallium, barium, calcium and copper oxide employing laser ablation in an oxidizing atmosphere, said method comprising:
laser ablating a target comprising thallium, optionally calcium, barium and copper oxides in a thallium and oxidizing atmosphere comprising an oxygen source in the presence of a target, whereby a plume of atoms is formed and directed to said target and said atoms impinge and bind to said target surface;
annealing under conditions to form a high temperature superconducting composition; and
cooling said atoms on said target surface to form a superconductive oxide layer.

18. A method for producing a superconducting article comprising an oriented superconducting layer of thallium, optionally calcium, barium and copper oxide, said layer being at least 30 Å thick and having a c-axis oriented normal to the crystalline substrate surface, said method comprising:
heating to an elevated temperature a mixture of thallium, optionally calcium, barium and copper oxides to form a liquid of an appropriate composition for formation of a crystalline superconductive layer;
immersing said crystalline substrate in said liquid at said elevated temperature;
cooling said liquid by from about 10 to 50°C or evaporating a portion of said liquid inducing crystallization of a superconductor and removing the main body of said liquid leaving a layer on said substrate.

19. A method for producing a superconducting article comprising an oriented superconducting layer of thallium, calcium, barium and copper oxide, said layer being at least 30 Å thick and having a c-axis oriented normal to the crystalline substrate surface, said method comprising:
coating said substrate with a first coating of a thallium and calcium oxide;
coating said first coating with a second coating comprising barium and copper oxide, wherein the atomic ratio is appropriate for formation of a superconductive layer;
heating said coatings to a liquefying temperature, whereby said thallium and calcium oxides form a liquid which dissolves said barium and copper oxides; and
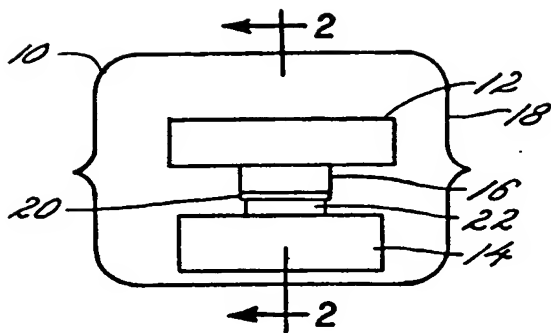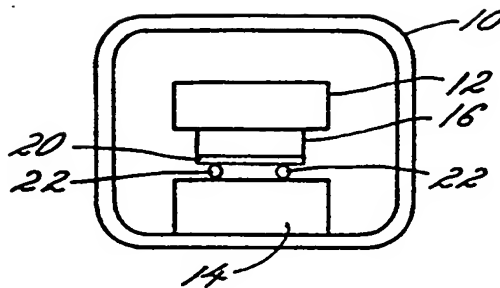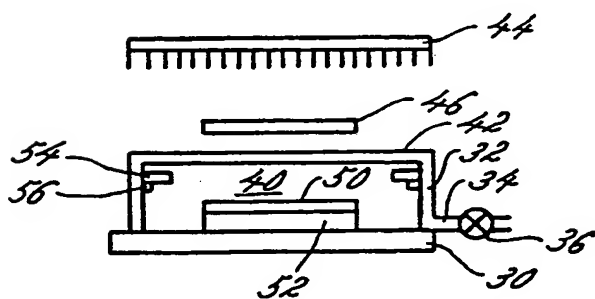cooling said liquid to form a superconductive layer.
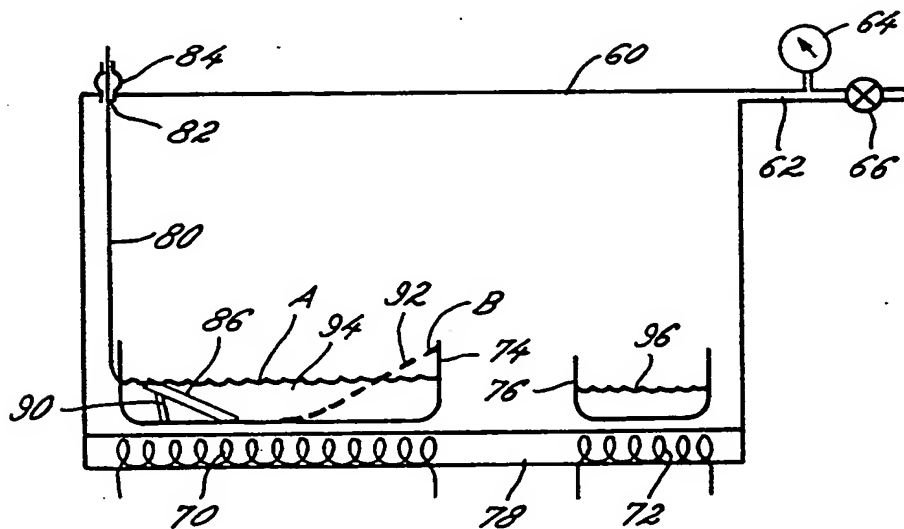
FIG. 1

FIG. 2

FIG. 3

FIG. 4
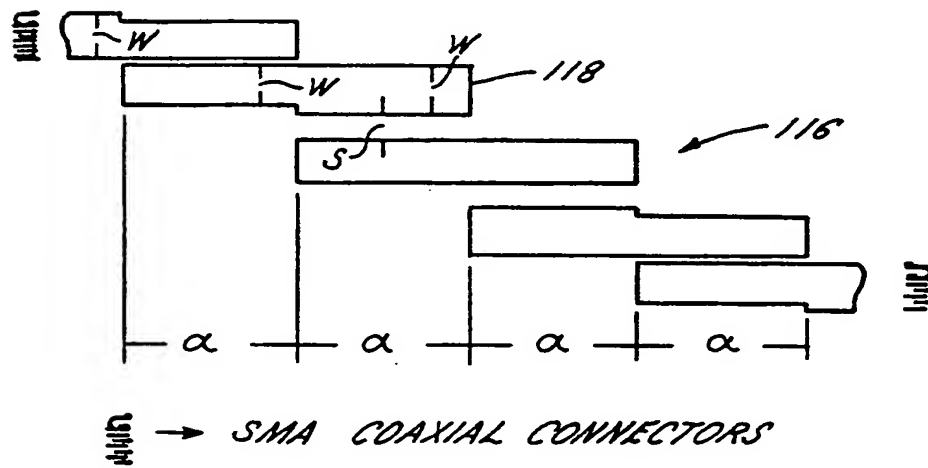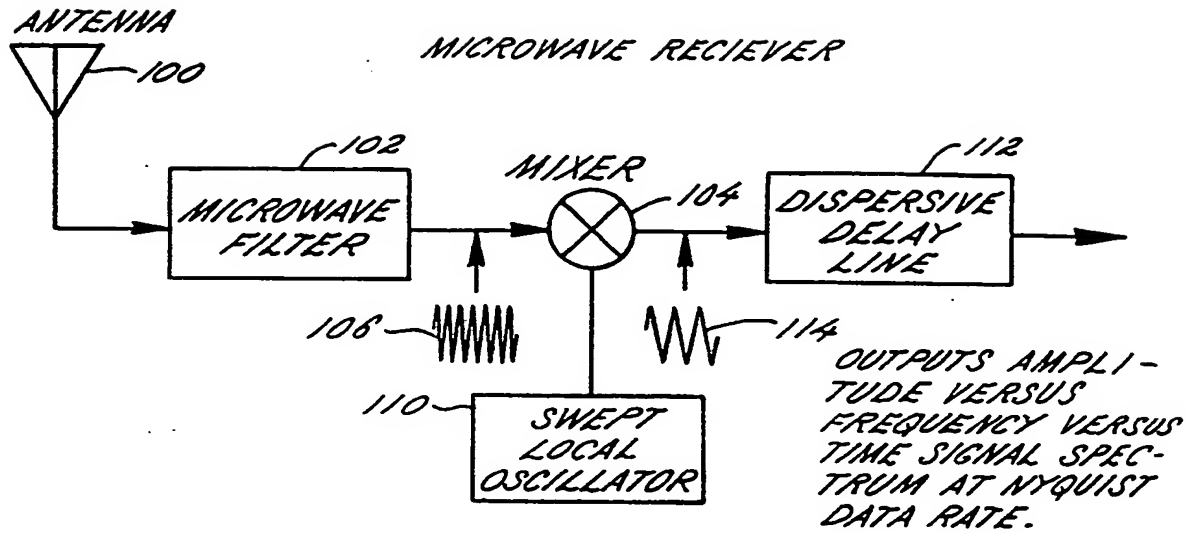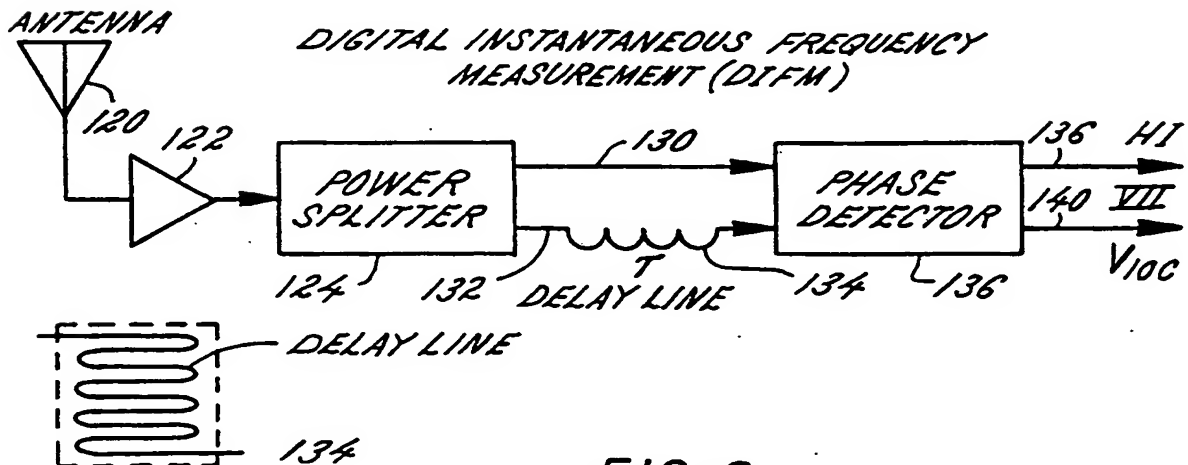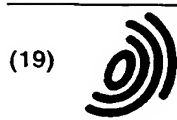
ANTENNA

MICROWAVE RECIEVER

100

102

MIXER

104

112

MICROWAVE FILTER

DISPERSIVE DELAY LINE

106

114

110

SWEPT LOCAL OSCILLATOR

OUTPUTS AMPLI-
TUDE VERSUS
FREQUENCY VERSUS
TIME SIGNAL SPEC-
TRUM AT NYQUIST
DATA RATE.

W

W

118

W

S

116

α   α   α   α

SMA COAXIAL CONNECTORS

FIG. 5

ANTENNA

DIGITAL INSTANTANEOUS FREQUENCY
MEASUREMENT (DIFM)

120   122

130

136   HI

POWER SPLITTER

PHASE DETECTOR

140   VII

124   132
DELAY LINE
T

134   136

V$_{IOC}$

DELAY LINE

134

FIG. 6

(12) **EUROPEAN PATENT SPECIFICATION**

(54) **Superconducting article containing thallium**

Supraleitendes Erzeugnis enthaltend Thallium

Article supraconducteur contenant du thallium

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(56) References cited:
DE-B- 2 532 570   US-A- 3 191 055

 • APPLIED PHYSICS LETTERS, vol. 53, no. 4,
  July 25, 1988 W.Y.LEE et al. "Supercon-ducting
  TlCaBaCuO thin films with zero resistance at
  temperatures of up to 120 K" pages 329-331
 • Nature vol.332 : March 3 1988, pages 138-139 ,
  Sheng and Hermann
 • Nature, Vol. 332, 10 March 1988, pages 138 - 139
 • Römpp Chemie Lexikon, 9. Auflage (1990),
  page 1195
 • Handbook of Thin Film Technology (1970),
  pages 4-10, 10-12, 10-17
 • Applied Physics Letters, vol.53, no.6, August 8,
  1988 I.SHIH et al. " Multilayer deposition of
  Ti-Ba-Ca-Cu-O films " pages 523-525 *Abstract
  page 523, left hand column, paragraph 2 - page
  524, right hand column, paragraph 1*
 • Applied Physics Letters, vol.53, no.4, July 25,
  1988 B.F.KIM et al. " Superconducting thin
  films of Bi-Sr-Ca-Cu-O obtained by laser
  ablation processing " pages 321-323

EP 0 357 507 B1

Description

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. application Serial N° 238,919, filed August 31, 1988, now issued as U.S. Patent N° 5 071 830 entitled "Metal Organic Composition Method for Forming Epitaxial Thallium-Based Copper Oxide Superconducting Films".

INTRODUCTION

Technical field

This invention concerns thallium based superconductors and devices employing such compositions.

Background

A recent scientific revolution in high temperature superconductivity has resulted from the discovery of many new metal oxide compounds, particularly copper oxide compounds, having dramatically increased superconducting transition temperatures (T_c). The initially discovered compounds were, for the most part, based on the combination of alkaline earth metals and rare earth metals, such as barium and yttrium in conjunction with copper. More recently, thallium based superconductors have been prepared, where the compositions have various stoichiometries of thellium, calcium, barium, copper and oxygen. The thallium materials have been more difficult to process, since the thallium Ca-Ba-Cu-O deposits are able to attain a composition which is liquid at processing temperatures. Thallium oxides have a relatively high vapor pressure at processing temperatures about 500°C and this has added to the difficulties in processing to ensure that the crystal structure has the correct stoichiometry. For the most part, sealed Au or Pt ampoules are used to control Tl volatilization by developing a controlled overpressure of Tl and oxygen above the film during high temperature processing.

Superconducting films are of great interest. However, in order to be useful, the films must be fairly uniform, be capable of carrying the current requirements of the device, have a superconducting transition temperature desirably aubstantially greater than the temperature of liquid nitrogen, have much lower RF surface resistance than copper, and be capable of reproducible preparation.

Relevant Literature

Ginley and co-workers at Sandia National Laboratories recently reported the preparation of superconducting thin films of the 2122 thallium compound (Tl_2, Ca, Ba_2, Cu_2, O_8). Jim Kwak at the same laboratory has reported polycrystalline thallium based films on yttria stabilized zirconia. Their films were prepared on yttria sta-

bilized zirconia substrates by sequential e-beam evaporation of the individual metals on the substrate, followed by a post deposition reaction step in a closed platinum crucible. The films that were obtained were unoriented and exhibited a transition temperature of 97K. IBM has reported preparing oriented thin films of the 2223 and 2122 compounds by rf diode sputtering.

A large number of articles have been published concerned with the thallium compounds. Illustrative of these articles are Sheng and Hermann, Nature, (1988) 332:55-58, generally disclosing TlCaBaCuO superconductors; Sheng and Hermann, Nature, (1988) 332:138-139, generally disclosing TlCaBaCuO superconductors; Ginley et al., Physica C, (1988) 152:217-222; Superconductor Week, Vol. 2, No. 18, May 9, 1988, reported that Sandia had prepared unoriented polycrystalline Tl thin films that have reached critical current densities of 110,000 A/cm^2 at 77K with a T_c at 97K. In the presence of a high magnetic field (6 Tesla), a critical current density of 1×10^6 A/cm^2 at 4K was observed.

Venkatesan et al., Appl. Phys. Lett. (1988) 52:1193-1195, and Wu et al., Proceedings of SPIE Symposium on High T_c Superconductors, Newport Beach, CA March 1988, report the use of pulsed laser deposition for preparation of high T_c superconducting thin films. Venkatesan et al., and Wu et al., supra claim to have achieved YBaCuO films that are superconducting after deposition at 650°C, followed by oxygen annealing at 450°C. Witanachchi et al., (Appl. Phys. Lett., in press) report that with the addition of DC bias plasma during laser ablation of high T_c superconducting YBaCuO thin films, in situ superconducting films can be achieved at substrate temperatures as low as 400°C. Lee et al, Applied Physics Letters, Vol. 53, No. 4, July 25, 1988, provides various characterizations and structural descriptions of thallium containing high temperature superconductors.

SUMMARY OF THE INVENTION

Superconducting thallium based films on substrates are provided, employing processes using growth from a liquid phase onto a crystalline substrate. Various techniques and conditions are provided to produce crystalline layers of superconductive material onto the substrate, obtaining epitaxial growth.

The products have superior superconductive properties as evidenced by surface impedance, with the products finding particular applications as components of electronic devices for microwave and millimeter wave applications.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagrammatic side view of a sealed vessel assembly for production of a superconductor film;
Fig. 2 is a cross section view along lines 2-2 of Fig. 1;

Fig. 3 is an alternate embodiment employing a device using infrared heat to produce a superconductor film;

Fig. 4 is a diagrammatic view of an alternate embodiment using a tilting vessel for coating a substrate with a superconductor film;

Fig. 5 is a schematic view of a narrow band microwave filter; and

Fig. 6 is a schematic view of a digital instantaneous frequency measurement device.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

Compositions and devices are provided comprising a thin film thallium based superconductor composition. The compositions comprise an average composition $Tl_a Ca_{n-1}, Ba_2 Cu_n O_{2n+4}$ as films on a variety of substrates, particularly crystalline substrates. Methods which have been employed to produce the films are both chemical and physical deposition techniques and include sol-gel and laser ablation techniques as preferred. The superconductor layer coated substrates find use as components in a wide variety of electronic devices, particularly with microwave and millimeter wave applications.

The films which are provided are primarily thallium-(calcium)-barium-copper oxides, with a stoichiometry which may include 2021, 2122, 2223, or such other stoichiometries as may be employed. The films will be oriented films, so as to have a substantially uniform crystallinity. The films may be comprised of a single crystal or a plurality of crystals joined at their grain boundaries. The films will be highly oriented with the c-axis substantially normal to the surface of the substrate as demonstrated by X-ray analysis or electron beam channeling techniques. For the most part, single phase films will be obtained, although, as desired, mixtures of two of the phases or related phases may be achieved within the film. For some applications polycrystalline films may be prepared.

The thickness of the film may be controlled. The film may be as thin as one layer, where the layer includes all of the necessary planes to obtain superconductivity, generally from about 30-50 °A, or may be as thick as two micrometers or greater, depending upon the particular application. The thickness of the film is primarily a practical consideration, rather than a significant limitation of the procedures employed.

For many uses, a fraction of a micrometer thickness will be employed, generally in the range of about 0.1 - 1μm. The film will have a superconducting transition temperature of at least 75K, more usually 90K, preferably at least about 100K, more preferably about 115K, and particularly preferred at least about 122K, where the transition temperature has so far been substantially less than about 150K. 2122 composition films can be achieved with a T_c of at least 110K and 2223 films with a T_c of at least 122K. The superconducting transition temperature should be as high as feasible, though in some situations one parameter may be compromised for another parameter. For the most part the films will be used at temperatures in the range of about 60 - 100K.

The films will usually have critical current densities at 77K of at least about 10^3 A/cm^2, usually at least about 10^6 A/cm^2. For microwave and millimeter wave applications, the surface resistance or impedance will generally be less than about $10^{-3}\Omega$, more usually less than about $10^{-4}\Omega$, at 10 GHz and at a temperature above 50K, preferably above about 75K.

The films will be substantially free of contaminants, having less than about 10 wt. %, preferably less than about 5 wt. % of material not involved with the superconducting crystal. For the most part, films will be at least about 0.5 cm as their smallest dimension and 3 cm or as large as 5 cm or more as their smallest dimension in the a,b plane.

The films will be of high quality as demonstrated by low lattice fault densities. By low lattice fault density is intended a sufficiently low fault density to demonstrate the intrinsic superconducting physical transport properties and sufficient to achieve required device property requirements. In addition, smooth surface morphologies can be achieved as well as uniform thickness. See Forsyth, Science (1988) 242:391-399, for a description of surface morphology of Nb_3Sn superconductors and the effect on electromagnetic properties.

Furthermore, the films may be grown epitaxially on substrates, where the crystal lattice of the superconductor does not differ by more than about 10% from that of the substrate. That is, along the a-axis of the crystal, the difference in lattice parameter between their a axes (($a_{s\text{-}ubstrate} - a_{superconductor})/a_{substrate}$) may differ by up to about 10% and still obtain epitaxial growth. However, with the subject film in addition to being highly oriented, one may also achieve epitaxy by appropriate choice of substrate.

Epitaxial Tl 2223 and 2122 films on {100} surfaces of MgO having intentional deviations of a few degrees from nominal orientation on axis can be beneficial. In a Tl 2223 film the <001> axis (lattice parameter, c = 36.26 A) is substantially coincident with the <001> axis of the MgO substrate or is at a systematic angular deviation in epitaxy with large lattice mismatches. Besides the correlation of the <001> axes, the epitaxial Tl film has its <100> and <010> axes parallel or at a systematic deviation to the analogous axes of the MgO substrate.

Various substrates including single crystal, polycrystalline, and amorphous substrates may be employed, depending upon the particular use for the coated substrate, whether one wishes epitaxy, the particular processing conditions, and the like. Substrates which may find use include magnesium oxide, yttria stabilized zirconia, sapphire, alumina, silicon, lanthanum aluminate, strontium titanate, gallium arsenide, lanthanum gallate, and calcium fluoride.

Various techniques may be employed for producing thallium based superconductors on a solid substrate.

Techniques which have been employed in the past with other superconductor metal oxide compositions include laser ablation, thermal evaporation, liquid phase epitaxy, electron beam, magnetron sputtering, and chemical vapor deposition. Illustrative of methods for producing the subject epitaxial layers are liquid phase thermal processing of sol-gel coating and laser ablation deposited coating.

Liquid phase film formation involves heating a deposited film to form a liquid coat on a substrate, whereupon the metal oxides crystallize from the liquid onto the substrate to form the superconductor layer. A liquid composition can be formed with Tl oxide, by itself or in combination with calcium oxide, as the solvent, with the other oxides becoming dissolved in the Tl oxide-containing liquid at an elevated temperature and subsequently crystallizing with the correct stoichiometry. Upon cooling, evaporation of the solvent, or chemical precipitation, the metal oxides crystallize to form a crystalline superconductor layer. Depending upon the substrate, the layer may also be epitaxial. One need not use the oxides initially, but can use metal compounds which may serve as the source of the metals in the liquid phase, where the counterions and conditions result in the formation of the desired oxide. The process may be divided into the following components: (1) Coating of the substrate; (2) Environment during crystallization; and (3) Thermal process conditions such as temperature, pressure, time; and (4) Miscellaneous other considerations.

For epitaxial growth, there will have to be pretreatment of the substrate to achieve consistent results. The liquid phase epitaxial procedure employs highly polished surfaces of the substrate. The surface may be polished mechanically or chemically, preferably both. Single crystal substrates are employed to obtain epitaxial film structures. For example, single crystal magnesium oxide <100> may be polished using hot concentrated phosphoric acid, for example, at about 80°C with 85% phosphoric acid for 10 min, or by lapping the surface flat and to the desired orientation and then immersing in conc. phosphoric acid at 50°C for 1-3 min. The resulting chemically polished crystal surface should be very clean, and provide a substantially defect free surface. The particular manner in which the surface is polished is not critical to this invention. Desirably, as exemplary of magnesium oxide, the (100) plane surface will be employed.

Coating of the substrate may be achieved in a variety of ways. One technique is to use chemical precursors, which upon pyrolysis may provide the desired oxide as a coating. Another technique is to employ a liquid comprising a solution of the metal oxides having an appropriate stoichiometry for production of the superconductor. Other techniques have been indicated, which involve vapor phase deposition. The first technique to be considered will be employing metallo-organic precursors to produce the oxides.

A sol composition is prepared employing metal soaps providing for the appropriate stoichiometry. The

soaps will be carboxylates of at least about 6 carbon atoms, preferably at least about 8 carbon atoms, and usually not more than 16 carbon atoms, more usually not more than 12 carbon atoms. Conveniently, the 2-ethylhexanoates have found use, although neodecanoates, or other branched chain, particularly alpha-branched chain fatty acids may be employed. The metal soaps are prepared in accordance with conventional procedures. The soaps are dispersed in an appropriate medium, particularly hydrocarbons or halohydrocarbons boiling in the range of about 40°C to 100°C, such as chloroform, toluene, xylene, benzene, methylenedichloride, etc., and the mixture made homogeneous by agitation, for example shaking, for several hours. Adjuvants may be added, such as thickeners, e.g. polysaccharides or ultra-high molecular weight polymers. The resulting solution and/or dispersion is then coated onto the substrate.

Coating can be achieved by putting the viscous sol onto the surface to be coated and spinning the surface by centrifugation for a short time to ensure the substantially uniform distribution of the film. Alternatively, the substrate may be dipped into or sprayed with the dispersion, protecting those areas of the substrate which are not to be coated. Any technique which allows for substantially uniform coating of the film on the substrate may be employed.

The coated substrate is then pyrolyzed for a short time at an elevated temperature, generally in the range of about 150°C to 500°C, preferably in the range of about 150°C to 300°C. Tl volatilization can occur at temperatures as low as 100°C, so that short process timing and Tl overpressures and oxidizing atmospheres are employed to control phase formation and to limit Tl loss and formation of undesired second phases in the film. The pyrolysis time and temperature should be selected to substantially ensure decomposition of the fatty acids, so as to leave a thin film of metal oxides, the pyrolysis occurring in the presence of oxygen, conveniently air. The procedure may be repeated as many times as desired, in order to enhance the thickness of the metal oxide film.

Desirably, each subsequent pyrolysis may be carried out at a lower temperature than the initial pyrolysis, where the initial pyrolysis is carried out in the upper portion of the temperature range, 250-450°C, and the subsequent pyrolyses are carried out at a temperature in the range of about 200-350°C. Usually, at least about 60% of the volatile organic material is removed and by extending the heating period, a constant weight can be realized. Care must be taken to minimize thallium volatilization when pyrolysing above 300°C.

The film, deposition and pyrolysis procedure will be carried out at least once, more usually twice, and may be five times or more, usually not more than about four times.

The thickness of each layer will depend upon a number of parameters: the viscosity of the sol, the time for spinning, the revolutions per minute, the temperature at which the substrate is spun, and the like. Where other

techniques are used to provide the coating, such as dipping, spraying, spreading with a blade, or the like, different parameters may be involved.

Once the substrate surface has been coated to the desired degree, the substrate may then be introduced into a closed inert vessel, containing pellets with the appropriate molar ratio for maintaining the stoichiometry of the film in the presence of a source of oxygen during heating. The molar ratio of the pellets is determined by the phase that is desired within the film. The film composition after heating is substantially affected by the geometry and temperature of the source material and the resulting Tl overpressure.

Maintenance of a controlled thallium overpressure may be achieved in a variety of ways. The simplest way may be to coat the layer containing the mixture of oxides with a thallium oxide layer, so that vaporization of the thallium oxide overcoat provides for thallium overpressure. To ensure sufficient thallium for incorporation in the superconductor layer, the housing for the thermal treatment of the superconductor layer should desirably be relatively small, so that a relatively small volume is occupied by the vapor. By relatively small is intended a volume of about 0.001 to 10 times the size of the substrate. In addition, compared to the surface of the superconductor layer, the surface of the thallium source should be relatively large, at least about one and a half times, preferably about two times, and maybe five times or more. In addition, the thallium oxide is desirably combined with calcium oxide and copper oxide, where the composition may be varied, depending upon whether the source is present during crystal growth or for stabilizing the thallium superconductor material after it is in the correct phase.

Conveniently, in the gas phase, air, pure oxygen, or other source of oxidizing oxygen may be employed, e.g., hydrogen peroxide or ozone during heating. The pellet composition will vary depending upon the particular thallium superconductor one wishes to prepare. For example, for the 2223 composition, the pellets will have a Tl: Ca: Ba: Cu 1:3:1:3 molar ratio. The inert tube is conveniently a passivated noble metal, most conveniently gold or plated quartz, which may be externally reinforced to support the pressures during the reactions.

The processing temperature will be at least about 600°C, more usually at least about 630°C, and not more than about 950°C, frequently in the range of about 800-900°C. The temperature may be monitored in any convenient way, conveniently a thermocouple. Usually, the temperature will be achieved rapidly, generally under five minutes, preferably under three minutes, more usually from about 0.5-3 minutes. Slower heating rates (20°C/min) may be employed to give continuous superconducting films of smaller grain size. The tube may be heated to a temperature or temperatures in the range indicated above, generally for sufficient time to ensure complete pyrolysis of any residual carbon compounds and allow for the atoms to assume the proper lattice

structure. Generally, the time at high temperature will be at least about 0.5 minute and not more than about 60 minutes, more usually in the range from about 0.5 to 25 minutes, preferably from about 0.5 to ten minutes. At the end of this time, the tube may be removed from the heating source and allowed to cool. Normally, there need not be any effort at rapid quenching, so that the tube may be allowed to sit in a room temperature environment, without providing for a rapid reduction in temperature.

A second preferred procedure for preparing the subject films employs laser ablation. Laser ablation can be used either to coat the substrate at room temperature in preparation for the thermal process described above, or can be used to deposit and form the superconducting phase in one step at elevated temperature.

Laser ablation is achieved by preparing an appropriate target. The apparatus for the most part, is conventional and is described in Wu et al, _supra_. A target is prepared by placing the appropriate composition of metals or metal oxides on the surface of a support which can be rotated at a controlled rate. The target on its support is placed in a vacuum chamber having a quartz window, where a laser beam of appropriate energy and wavelength impinges on the target causing a plume of ablated vapor normal to the target suface. The substrate is placed substantially normal to the direction of the plume, so as to receive the atoms in the plume, where the atoms bind to the surface of the substrate. The substrate is maintained at room temperature or at an elevated temperature depending on whether the goal is an amorphous or a crystalline deposit.

The laser ablation target can conveniently be made in the same manner as the sol-gel coating described earlier. Thus, a uniform film of the various carboxylates can be prepared and pyrolyzed as described previously to produce the desired oxide mixture. Pyrolysis can be carried out in the presence of oxygen, so as to ensure the formation of the desired metal oxides in their proper oxidation state. Alternatively, the target can be made from pressed and sintered powder or from hot pressed powder.

The laser energy density on the target will generally be from about 1-3 J/cm^2. The film on the target will have the same metal molar ratio as the intended composition on the substrate 1 cm^2 to 63 cm^2 in surface area and about 25μ to .7 cm thickness.

The laser may be focused to cover various areas of the target. The laser may impinge upon the surface over a wide range of angles from a minimum of about 2° up to 90°. A typical impingement angle is about 25°. The area impinged by the laser will generally be at least about 2 mm^2 and not more than about 50 mm^2. A typical area is about 15 mm^2. The ratio of length to width will depend upon the angle of impingement, and will generally be at least 2 to 1, and not more than about 20 to 1, more usually not more than about 10 to 1. By employing an energy in the range of about 2 J/cm^2 per pulse, one can deposit about one monolayer, generally about 3×10^{-10}m thick

onto the substrate with each pulse. By controlling the number of pulses per second, which would generally range from about 0.5 to 50, one can achieve an accretion on the substrate of about 0.1 μm/min.

The target will usually be relatively close to the substrate, usually not less than about 2cm and not more than about 10 cm, preferably about 6 cm. The chamber will be evacuated to under about 500mTorr, preferably from about 2 to 200mTorr, more preferably about 100 to 200mTorr. Various inorganic oxidizing gases may be present, such as oxygen, air, hydrogen peroxide, ozone, nitrogen oxides, such as nitrous oxide or the like, where the inorganic oxygen source can be activated by virtue of the laser beam or an independent energy source. For example, an oxidizing gas source may be directed toward the layer on the substrate where the gas has been activated, for example, oxygen activated by passing through an electric field or laser.

For growth of crystalline superconducting films the substrate will generally be maintained at a temperature in the range of about 450-750°C, preferably about 500-650°C. The temperatures which are maintained will allow for the atoms to form the proper crystal structure, but should be kept as low as possible to minimize interdiffusion between the film and substrate and to minimize thallium loss by vaporization. The lower the temperature which is used for the substrate, the slower the deposition rate which should be employed. Alternatively, one can increase the energy of the atoms and molecules in the plume by providing for a plasma in the ablated plume. This additional energy increases the atoms' ability to form the proper crystal structure at low temperature, and increases the rate at which the film may be grown.

In some instances, where thallium may be lost because of its higher vapor pressure, it may be desirable to increase the amount of thallium in the target. Alternatively, thallium loss can be minimized by maintaining a higher oxidation potential in the apparatus.

It may be desirable to sequentially ablate one or a combination of metals or metal oxides, so that layers of different composition are deposited sequentially to provide the different atomic layers of the crystal.

Besides deposition on elevated temperature substrates as described above, laser ablation can be used to deposit onto room temperature substrates prior to thermal processing. Laser ablated films on room temperature substrates are dense, uniform and high purity, but are not crystalline. These amorphous films, when heated, form liquid and then solid crystalline phases in the manner previously described for chemical processing. The kinetics of liquid phase formation is somewhat different for the two kinds of films because the chemically prepared films tend to be highly porous, and may contain some residual carbon before thermal processing.

Layers of different composition may be employed. Of particular interest is having an initial layer of thallium oxide, preferably a combination of thallium oxide and calcium oxide, with a second layer comprising at least copper and barium oxides, desirably comprising thallium and calcium oxides as well. These layers can be achieved as described above, using the various processes which allow for the independent application of different compositions as layers on the substrate. For example, with the sol-gel technique, one could first provide for a layer of thallium and calcium carboxylates, which may or may not be pyrolysed prior to coating with a layer of carboxylates of all of the metals.

An alternative procedure for coating the substrate, may employ the physical method of tilting. By employing a boat which can be tilted, so that the liquid composition can be kept away from the substrate, a liquid of the various oxides may be produced. Once the liquid is formed, the boat may be tilted, so that the liquid now coats the substrate, which is in the other part of the boat. Desirably, the substrate may be positioned, so it is at an angle to the bottom of the boat, with the higher end near the wall of the boat. The conditions under which the coating is carried out would provide for a rapid rise to a temperature in the range of about 500 to 880°C, at which point the oxides would be in the liquid form. The boat can then be tilted and cooling begun at a relatively slow rate, in the range of about 0.5-10°C/min until the temperature has dropped at least about 10°C, preferably not more than about 50°C, when the temperature is in the range of about 490-860°C. At this point, the boat would be tilted back to the original position, where the substrate was no longer in the liquid, and the substrate would be rapidly cooled at a rate of at least about 10°C/min, preferably at least about 20°C/min to room temperature.

Various configurations may be employed during thermal processing between the source and the superconductor film. The source should not be allowed to contact the superconductor film. The configurations may allow for the source being in a confronting relationship to the superconductor film. For example, a substrate coated with the source may be spaced from the substrate coated with the superconductor film by a spacer (typically 5 microns or greater in thickness), where the source and film are in a confronting relationship.

An alternative configuration would have the superconducting film on a substrate in a container, where the source is displaced from the superconductor film and is maintained at a temperature differential from the superconductor film. Thus, by varying the temperature of the source, different thallium overpressures would be achieved, so as to ensure the proper Tl stoichiometry at the superconductor film surface.

Various regimens may be employed for producing these superconducting films and for use in a postannealing of the superconducting material. By employing schedules for heating and pressure that inhibit the evaporation or boiling of the liquid in the film prior to formation (precipitation) of the superconducting material, one can provide for condensation of Tl source material, so as to provide for precipitation of the superconducting phase, and can minimize or prevent the formation of nonsuper-

conducting oxide compositions.

One protocol would initially provide for a pressure of about 3 atm with a rapid rise in temperature from room temperature to 850°C, at about 50°C/sec rise, so that the temperature is reached in about 15 to 20 sec, maintaining the superconducting film at this temperature, where approximately 100 sec will have elapsed from the initiation of heating, allowing the superconductor to cool over a period of about 5 to 10 sec to a temperature of about 550°C and maintaining the temperature for an additional 100 sec, followed by cooling to room temperature. During this time, a different heating profile is employed for the source material, where the source is heated at about the same rate along with the superconductor film, but is maintained at the high temperature for about 5 to 25 sec longer than the superconducting film, so that the overpressure is maintained relatively constant while the superconducting film is undergoing its initial cooling, followed by dropping the source temperature by about 100°C and maintaining this temperature during the annealing of the superconducting layer. The temperature is then allowed to drop to room temperature along with the superconductor layer. The pressure profile would be to maintain the elevated pressure until the annealing temperature has been reached and then allow the pressure to drop to 1 atm.

Where the source and superconducting layer are both maintained at the same temperature, a different protocol would provide for heating at about 40 to 70°C/min to 800°C, where the temperature is achieved in from about 15 to 40 sec, preferably about 20 to 30 sec, while maintaining an oxygen pressure at 3 atm. The elevated temperature is maintained for an additional 60 sec and then reduced at a temperature drop from about 5 to 20°C/sec to room temperature. The pressure profile differs in being maintained at the elevated pressure for about 60 sec, and then allowed to drop to 1 atm over about 10 to 20 sec. By adjusting the liquid composition, growth may be achieved at one atm pressure.

Parameters for a thermal anneal will vary from the preparation of the superconducting film. For the anneal, the superconducting film is rapidly heated to a temperature in the range of about 500 to 750°C, generally over a period of about 10 to 30 sec. The temperature will then be maintained, ± 15% for a period of about 5 to 60 min, preferably from about 15 to 45 min in an oxygen atmosphere while in the presence of a thallium source. The temperature for the source will be higher by at least about 50°C, preferably from about 100 to 150°C higher than the superconducting film. The temperature of the source will be heated analogously to the superconducting film, so that the ultimate temperature for the source is reached at or shortly after the temperature for the film is reached. The temperature for the source will be maintained substantially constant during the period of annealing and will then be allowed to cool at about the same time as the superconducting film back to room temperature, as well as at about the same rate. Desirably, cooling of the

source will begin shortly before the cooling of the superconducting film, usually from about 0.5 to 5 min prior. During the annealing, an elevated pressure may be employed, usually about 1.5 to about 2.5 atm, preferably up to about 2 atm.

Localized effects can be achieved by employing infrared heating. For example, the substrate with the pre-superconductor or precursor film could be placed in an enclosure having an infrared transparent window above the film and having a small volume relative to the substrate. By employing infrared heat, vaporization would occur in a small volume with a rapid increase in pressure. Furthermore, the assembly could be introduced into a pressure vessel, which would also have an infrared transparent window, so that the entire assembly could be pressurized. In this way, the gas environment in which the superconductor film is formed would be rapidly saturated with thallium oxide vapor. The process may be carried out at atmospheric or superatmospheric pressure.

By placing the substrate on a large thermal mass base, and using infrared heating, a heat flux will occur at the substrate precursor film interface, since the substrate will have higher thermal conductivity than the precursor or the intermediate liquid composition. Thus, there will be a temperature gradient in the film and substrate, where the precursor film will be at a higher temperature than the substrate. The cooler substrate can then provide a site of nucleation for the formation of the superconductor film.

For further understanding of the invention, the drawings will now be considered. In Figures 1 and 2 are depicted different views of tubular devices and arrangements for production of superconductor films. The gold sealed vessel 10 houses thallium pellet sources 12 and 14. A substrate 16 separates pellet 12 from the superconductor layer precursor 20. A wire horseshoe spacer 22 prevents the pellet source 14 from touching the superconductor layer 20. Prior to sealing tube 10, the various components may be assembled to provide the indicated assembly and introduced into the housing 10. The housing may then be sealed and introduced into a furnace where it is rapidly heated to the desired temperature and maintained at that temperature. However, it is not necessary to seal the pouch in order to prepare high quality films using this process geometry. Usually, a small amount of air or oxygen will be allowed to remain in the sealed housing 10. Upon heating, the pellet sources will partially evaporate, so as to maintain a thallium oxide overpressure in the housing 10, to prevent significant evaporation of thallium oxide from the superconductor precursor layer. After sufficient time for the superconductor layer to form, the tube may be allowed to cool by turning off the furnace and letting the furnace chamber come to room temperature.

In Figure 3, an alternative embodiment is provided, where infrared heat is employed to produce the desired temperature. Mounted on a base 30 is cover 32 having

conduit 34 and valve 36 for evacuating or pressurizing the chamber 40. The cover 32 has an infrared transparent ceiling 42 to allow for transmission of infrared rays into chamber 40. An infrared source 44 is provided which is able to irradiate the entire chamber. A removable mask 46 is provided which when in place prevents radiation from heating the superconductor film precursor 50. The superconductor film precursor 50 is coated onto substrate 52 which sits on base 30. A thallium oxide ring 54 is mounted on support 56 inside the chamber, where the thallium ring will be exposed to the infrared radiation when the mask is in its position.

In preparing a superconductor film, one would place the substrate 52 coated with the superconductor precursor film 50 onto the base 30 and then mount the cover 32 on the base. The chamber may then be filled with oxygen and irradiation with the infrared lamp 44 begun, with the mask in place. When a sufficient thallium oxide partial pressure has been achieved, the mask may be removed and the precursor film 50 heated to an elevated temperature, so as to provide for formation of the superconductor film. After sufficient heating, the lamp 44 may be turned off, the chamber 40 allowed to cool to room temperature, evacuated, and the cover removed for isolation of the superconductor film.

In Figure 4, an alternative embodiment is indicated, where one or more substrates may be coated with a superconductor film precursor, where the substrate may be repetitively coated, until a layer of the desired thickness has been achieved. A housing 60 is provided having conduit 62 with pressure gauge 64 and valve 66. The base of the housing 60 has two heaters, 70 and 72 which can provide heat to vessels 74 and 76 respectively. Attached to one end of vessel 74 is rod 80 which extends through orifice 82 outside of housing 60. Seal 84 prevents the introduction of air or loss of vapors into housing 60. Substrate 86 is situated in vessel 74 supported at an angle by mount 90. By means of rod 80, vessel 74 may be moved from position A, where the surface of the liquid precursor to the superconductor film is substantially parallel to the base 78 of housing 60. In this position, the substrate 86 is immersed in the superconductor precursor liquid. By lowering the temperature or evaporating some of the solvent, crystallization of a superconductor film on the substrate is induced. By raising the rod 80, or tilting the entire apparatus, one can then move the liquid to position 92 indicated by the broken lines B, so that the substrate 86 and superconductor film is no longer coated with the superconductor precursor liquid 94. Vessel 76 will contain thallium oxide liquid 96 which may serve to provide a thallium oxide overpressure in the housing 60. The temperature of the thallium oxide liquid 96 may be maintained at a lower temperature from the superconductor precursor liquid, since it will be solely comprised of thallium oxide, and can be used to control the overpressure in the housing 60.

The subject device components can be used in a wide variety of devices. Because superconductive layers have low microwave surface impedance, they find use in numerous microwave and millimeter wave applications. The subject elements comprising the substrate and film, by appropriate choice of substrates, may find use in radio frequency cavities and resonators, microwave shielding, antennas, in transmission lines, employing different structures, such as coaxial, microstrip, coplanar wave guide, coplanar strip line, inverted or suspended microstrip, and the like. The devices find use in signal communications or delays, filters, resonators and oscillators, circuit interconnections, power combiners, and antenna feeds.

For a narrowband microwave filter with superconducting resonator elements, the specifications could be:

Transmission medium: microstrip coupled lines (5-15 resonator elements)
Bandwidth: 0.1-10% at the center frequency (f_o)
Dimensions:

Superconductor thickness (t)=1 micron
Relative dielectric constant
(ϵ_r)=9.65 (MgO)
Loss tangent=.0002 (MgO)
Substrate height (h)=0,635 mm (25 mils)
Spacing (s)= 0,254 - 3,81 mm (10-150 mils)
Line width (w)= 0,0254 - 1,016 mm (1-40 mils)
Length (l), 0.25 guide wavelength at f_o, l=2,90 mm (114 mils) at 10GHz

Package dimensions:

X=25 mm (1in.)
Y=25 mm (1in.)
Z=6,25 mm (0,25in).

The filter is packaged in a shielded case and cooled to 77°K and connected with an SMA coaxial connector to other hardware part.

An exemplary narrow band microwave filter with superconducting resonator elements is depicted in Figure 5. The filter comprises antenna 100 which feeds the signal to microwave filter 102. The signal from microwave filter 102 is fed to mixer 104 in conjunction with signal 106. A swept local oscillator 110 also feeds a signal into the mixer 104, which provides an output to dispersive delay line 112 in conjunction with signal 114. The superconducting resonator elements 116 are shown in an array where "w" is line width, "s" is spacing and "l" is length. The low loss of the narrow band microwave filter enables the microwave receiver to have a relatively higher signal to noise ratio. The dispersive delay line is used to process long pulses (higher energy) as if they were short pulses (higher range resolution). First described by R.H. Dicke, U.S. Patent No. 2,624,876, issued January 6, 1953.

Delay lines are an integral part of a digital instantaneous frequency measurement (DIFM) component. The

delay line specifications could be as follows:

Dimensions:

Superconductor thickness (t)=0.015 μm - 2 μm
ε$_r$=9.65 (MgO)
Loss tangent=0.0002 (MgO)
Substrate height (h)=0,635 mm
Line width (w) = 1 μm - 1 mm (0.04 - 40 mils)
Total length (1)=20 mm

Package dimensions:

X=25 mm (1 in.)
Y=25mm (1 in.)
Z=6,25 mm (0,25 in.).

The delay line can be packaged in a shielded case thermally attached to a 77°K cold finger with SMA coaxial connectors interconnecting the delay line within the DIFM.

A digital instantaneous frequency measurement is diagrammatically depicted in Figure 6. The antenna 120 feeds a signal to a diode 122 which feeds the signal to power splitter 124. The power splitter 124 outputs directly to phase detector 126 through lines 130 and 132 which comprises delay line 134 comprised of the superconductor film. The outputs of lines 130 and 132 are fed into phase detector 126, which then outputs signals 136 and 140 to video 142.

The following examples are offered by way of illustration and not by way of limitation.

EXPERIMENTAL

The individual Tl, Ca, Ba and Cu metal carboxylate compounds were prepared following established procedures. The resulting solutions of metal soap compounds in chloroform were reduced in volume by evaporation and analyzed by atomic absorption for their metal contents. These precursor solutions were then used to prepare the precursor sol by combining 5g copper 2-ethylhexanoate, 3.29g barium 2-ethylhexanoate, 3.14g calcium 2-ethylhexanoate, and 8.462g thallium 2-ethylhexanoate in 5 ml of chloroform. The precursor stoichiometry was Tl$_2$Ca$_2$Ba$_2$Cu$_3$. The solution was mixed by shaking for several hours. This precursor solution was spun onto a single crystal yttria-stabilized zirconia (<100> orientation) substrate at 4000 rpm for 30 sec followed by pyrolysis at 400°C for 5 min. This spin/pyrolysis procedure was repeated twice more at 250°C. Oxide pellets with a molar ratio Tl:Ca:Ba:Cu-1:3:1:3 were prepared by mixing the individual oxides together by grinding and then pressing uniaxially in a Carver press. The pellets and the coated substrate were placed in air in a 6.25 mm $\frac{1}{4}$ diameter gold tube and hermetically sealed. The

sealed gold tube was attached to a thermocouple probe using wire and inserted into a preheated tube furnace. The material was brought to a temperature of 855°C in 2 min and held for 10 min. The sample was then removed from the furnace and cooled to room temperature. The entire film processing procedure required about 15 min to complete.

Optical micrographs of the pyrolyzed film revealed the presence of a large number of plate and needle-like (plate on edge) structures throughout the film. Both structures were found to have, by energy dispersive x-ray analysis, the 2223 composition. Scanning election microscopy of the film showed the plate-like morphology of the superconducting 2223 compound. The micrograph also showed the spherical Ca/Tl oxide deposits that inhabit regions immediately adjacent to the plate-like structures. The composition of the plate was determined by SEM-EDX (scanning electron microscopy energy dispersion x-ray spectroscopy) to consist of 12 atomic percent Ba, 12 Tl, 12 Ca and 20 Cu. The compositional analysis results were consistent from area to area and are consistent with the material possessing a 2223 metal stoichiometry. The highly oriented nature of the 2223 film is indicated by the large enhancement of the <001> reflections in an x-ray diffraction scan. A minor peak at 6° was indicative of a very small amount of the 2122 phase in the film. The temperature dependent magnetic susceptibility measurement was performed on the film on the assumption that the material consisted of a 2 micron thick fully dense film. It was calculated that greater than 60% of the material became superconductive.

To prepare the 2122 composition, the above procedure was repeated, except the composition of the source material corresponded to a Tl:Ca:Ba:Cu atomic ratio of 2:2:2:3. The temperature was slightly modified to 860°C for reaction and the substrate which was employed was a magnesium oxide substrate single crystal that had been chemically polished using hot concentrated phosphoric acid as described previously (See Sanywal and Sutaria, J. Mater. Sci. (1976) 11:2271-2282) to provide a substantially defect free (<100>) surface.

Optical micrographs of the pyrolyzed film revealed the presence of a large number of plate-like structures throughout the film. These structures were found by SEM-EDX to have a chemical composition corresponding to the 2122 material. SEM of the film clearly showed the plate-like morphology of the superconducting 2122 compound. The film was highly c-oriented as indicated by highly enhanced <001> reflections. The film was found to be epitaxial by comparing electron channeling patterns of the single crystal substrate with that of the film in various regions. The morphology of the film is strongly indicative of the presence of an intermediate liquid phase during processing. The surface of the film (which resembles thin film surfaces obtained by liquid phase epitaxial growth techniques), was analyzed by EDX to have the correct cation stoichiometry for the 2122

compound.

Electron beam channeling patterns were obtained from many representative areas within the film. Electron channeling patterns of the film revealed that the orientation of the a, b plane within the 2122 film was identical to that of the substrate in many areas throughout the film. In a few areas, the channeling pattern of the film was slightly misoriented (by a constant amount) from the substrate, perhaps indicative of a buildup of strain or dislocations at the film/substrate interface due to lattice mismatch which is approximately 9%. The lattice registry with the surface was maintained not only at layers close to the magnesium oxide substrate, but also at the top of plates many microns from the substrate surface.

To deposit a thallium-based superconducting film by PVD, for example of the 2223 composition, a substrate is loaded into a specially designed vacuum chamber, and held in position where it faces a target approximately 6 cm away. The vacuum chamber is evacuated to a pressure of less than 1×10^{-6} torr, then back filled to 5×10^{-3} torr with oxygen, while the substrate is heated to a temperature between room temperature and 400°C. Material is then vapor transported from the target to the substrate by laser ablation, using a laser energy density on the target of 1.5 to 2.0 Joules/cm^2. The laser is pulsed at 5Hz for 5 to 10 minutes, depositing a film 0.5 to 1.0 μm thick. After ablation, the film is cooled to room temperature and the substrate removed from the vacuum chamber.

The film thus deposited is continuous and smooth over the entire substrate. In some locations there are particles on the film surface that appear to have been transported from the target either in solid particle form or as small melted globules. The film composition, measured by energy dispersive x-ray (EDX) spectroscopy, is found to be the same as the target composition for substrate temperatures up to 400°C. Thus if the target has the 2223 composition, the film has the same composition. When the substrate temperature is 600°C, the maximum content of the film is lower than that of the substrate because the film loses thallium by evaporation. The loss can be compensated by increasing the thallium content of the target.

The films are not superconducting as deposited, but become superconducting after annealing at 750-850°C in a gold pouch containing a source of thallium vapor.

An additional number of preparations were carried out using a variety of substrates. The substrates include polycrystalline forms of magnesium oxide, zirconia and alumina, as well as single crystal sapphire. The films are prepared by coating a chloroform solution of Tl, Ca, Ba and Cu 2-ethylhexanoates onto the substrate and pyrolyzing the film at 250°C. This process is repeated up to as many as 10 or more times to develop the desired thickness prior to high temperature processing. A film thickness of 5μ is obtained after coating a substrate three times.

The chemically deposited films are prepared by first coating cleaned substrates three times as described above. The prepyrolyzed film is amorphous by XRD and TEM. The film consists of an intimate mixture of the metal ions, where the Tl, Ca stoichiometry of the film prior to high temperature pyrolysis has not been found to be particularly critical to producing the high temperature superconductor (HTSC) material. However, if excess Ba and Cu are added, large hexagonal crystals of barium cuprate are produced during high temperature pyrolysis.

High temperature thermal processing is carried out using the following procedure. The initially amorphous chemically deposited film is placed between two source pellets. The source materials are typically 12.5 mm (1/2 inch) diameter uniaxially pressed powder compacts of Tl-Ca-Ba-Cu oxides. The stoichiometry of the source material plays a critical role in determining the phase(s) that are produced during processing. The two most common source compositions that are used are Tl-Ca-Ba-Cu ratios of 1313 and 2223. A spacer is placed between the pellets and a film inserted between them. The film surface is prevented from touching the surface of the pellet through the use of a ceramic or metal spacer. It is important to prevent contact of the film with the source material in order to obtain morphologically uniform films over large areas (>1cm^2). Contact of the film with the source material often destroys the uniformity and integrity of the final fired film.

The source/film structure is inserted into a preconditioned gold tube. The gold tube is then purged with air, nitrogen or oxygen, and closed (hermetic seal is not necessary). The material is then heated to a final temperature ranging between 600° and 910°C. The heating rate that is employed is important. Slow heating rates ranging from 10-30°C/min usually produce polycrystalline, unoriented films that range in thickness from 2-10 microns. Faster heating rates produce oriented films. The typical range of heating rates used to produce oriented films is between 50-500°C/min. The higher heating rates are obtained by placing the gold pouch directly into a preheated tube furnace and monitoring its temperature by using a thermocouple inserted directly into the pouch. The film orientation that is obtained upon rapid heating of chemically deposited films is largely the c-axis of the material normal to the substrate surface. Rocking curves as sharp as 0.3 degrees have been obtained for such materials. Some evidence for nucleation of material with its C-axis parallel to the substrate has also been observed; however this material represents a small volume fraction of any particular film. Epitaxy has been demonstrated for single crystal MgO substrates.

The degree of orientation of the film is intimately related to the phase formation process. The intermediate liquid phase that is obtained during high temperature processing plays a key role in controlling the morphology, phase identity and purity, crystallographic orientation and density of the film. The studies show that the intermediate liquid phase obtained consists primarily of Tl and Ca oxide at low temperature (ca., 600°C). Large

grains of the 2-layer material have been observed at temperatures as low as 650°C for rapidly heated samples, indicating that liquid phase formation is indeed occurring at these relatively low temperatures. DSC experiments on pyrolyzed chemical precursors corroborate these findings. Slow heating rates (i.e., 10°C/min) result in a relatively small amount of liquid phase (per unit volume) being produced in the film and a large number of nucleation sites within the film. These factors combine to produce fine grained material (<5 microns) exhibiting a very low degree of crystallographic orientation. The nucleation is random in orientation and occurs throughout the deposit, resulting in a randomly interconnected platelet structure of the superconducting material. The coverage of the film on the substrate is excellent and uniform - apart from the fact that the film is a fairly porous network of 5 micron grains of material. A surface resistance measurement of a polycrystalline film on single crystal MgO revealed that the material had a reasonably low loss with a surface impedance that was approximately a factor of two greater than cryogenic copper at 50K and 10 GHz.

On the other hand, rapid heating rates (>50°C/min) produce a markedly different film morphology. During rapid heating of the precursor film, a large volume fraction of liquid phase is produced. The liquid, which initially consists primarily of Tl and Ca oxides, rapidly dissolves any barium and copper in contact with it and directly precipitates out the 2122 or 2223 compound. The liquid phase is very mobile and formed early in the heating process. Material transport via this intermediate liquid phase is extremely rapid. Thus an initially porous 5 micron (low initial density) thick film can shrink in thickness to just over 1 micron during processing. The phase that is produced from the liquid depends upon the overpressure that is in equilibrium with the liquid. The use of source materials that contain the 2223 phase (or produce it during the anneal experiment) will typically result in films that contain the 2223 phase. The local thallium overpressure is important to determining the phase that is produced from the liquid. If the overpressure is too low, no superconducting material is obtained.

The degree of crystallographic orientation of the film can be readily controlled through appropriate selection of the film process condition. By employing heating rates between 20 and 50°C/min (the end regimes for polycrystalline and oriented/epitaxial film growth), partially oriented films exhibiting a range of morphologies, densities, and thicknesses can be obtained.

Sharp superconducting transitions have been obtained for 2 layer films both by resistivity measurements (R=0 at 107K) and AC susceptibility. An oriented 2122 film produced by this process on single crystal MgO has apparently the lowest surface resistance at 77K of any HTC film or bulk material that has been reported. This material was oriented and, perhaps, epitaxially related to the substrate. Films prepared using the same processing parameters were found to exhibit very sharp x-ray

rocking curves; typically less than 0.7 degree full width at half maximum (FWHM). Values as low as 0.3 degrees were also obtained. This value is comparable to the best rocking curve data that have been reported for HTSC thin films of any material. Additionally, further improvement may be achieved with optimization of this process.

For rapid thermal annealing of films with a Tl overcoat, the following experiment was performed. A coating of Tl 2-ethylhexanoate was spun onto a prefixed film containing the oxides of Ca, Ba and Cu. The initial film was prepared by firing a normal stoichiometry film (2223) in a Tl overpressure insufficient to prevent complete vaporization of Tl from the sample. A total of three Tl overcoats were added followed by firing in an oxygen atmosphere at 860°C in a sealed gold pouch. A source pellet was included in the pouch to control the Tl overpressure. After processing, the film contained a large amount of 3-layer superconducting material.

In the next experiment, a 2223 mixture of the appropriate metal cations was dissolved in nitric acid and the solution evaporated onto a single crystal MgO substrate. This material was dried in a box furnace at 80°C and fired in a gold pouch using the normal procedure. The 2122 compound was formed from the thermally processed nitrate precursor. The morphology and composition of a number of areas of the film (SEM-EDX) were entirely consistent with the presence of the 2122 material. Other solutions or colloidal dispersions that may be used to deposit precursor films include carbonates, citrates, hydroxides, fluorides, chlorides, and acetates of these metal ions. Tl, Ca, Ba or Cu salts can share the same counterion (i.e., all be chloride salts), or consist of various complex mixtures of different anions. The precursors are fired under the appropriate conditions to complete phase formation and removal of the counterions (i.e., removal of halides requires heating under a water-containing atmosphere, oxygen atmosphere for organics).

Studies have conclusively shown that the intermediate liquid phase that was used to engineer the morphology and properties of the films can be very reactive with a number of different materials of technological interest. Direct physical contact of the partial melt produced within the film can result in degradation of the superconducting material; particularly on substrates such as sapphire or polycrystalline alumina. Often after processing the films on Al-containing substrates the presence of barium-aluminate crystallites in the film has been observed. The obvious corrosion of single crystal plates of the 2122 or 2223 compound that were produced early on during thermal processing but were subsequently dissolved by contact with liquid during processing to degrade the material were noted.

Superconducting Tl films on sapphire substrates are produced without interference from the substrate by employing the following technique. The first is to fire the film using an intermediate heating rate (approximately 50°C/min) that effectively serves to limit the amount of

liquid phase that is present at any particular time during the process. The second is to limit the substrate reaction by reducing the amount of time the material is at high temperature. Both of these techniques have been demonstrated in the laboratory to be successful for controlling deleterious substrate reactions of the 2122 or 2223 phases on sapphire substrates.

Other than lowering the temperature or shortening the time at temperature, another method for reducing substrate reaction is to deposit a barrier layer onto the troublesome substrate material. MgO and Y-stabilized zirconia as buffer layer materials on sapphire, silicon and gallium arsenide substrates may be employed. Zirconia (yttria stabilized) and magnesium oxide demonstrated phase compatibility with these materials under the subject current process conditions. The buffer layer material can either be epitaxial or polycrystalline.

A number of preparations were carried out using the following experimental procedure.

The metal 2-ethylhexanoate precursor solutions were prepared using standard published synthetic procedures. The film itself was generated by spinning a solution prepared from copper 2-ethylhexanoate, barium 2-ethyl hexanoate, calcium 2-ethylhexanoate and thallium 2-ethylhexanoate onto the appropriate substrate. The film thickness was adjusted by controlling solution viscosity, spin speed, spin time and number of coats. Typically the substrate was spun at 3000 rpm for 30 sec. After each precursor coat, the film was fired at 250°C for 6 min to pyrolyse the 2-ethylhexanoate. This was repeated three times to build up sufficient thickness of the precursor material.

The pyrolysed films were loaded into gold pouches containing oxide pellets of known stoichiometry (for example Tl/1: Ca/3: Ba/1: Cu/3) and compression sealed. Both air and oxygen atmospheres have successfully produced the superconducting phase. The charged gold capsule was heated in a horizontal tube furnace at a temperature ranging from 750°C to 920°C and for times from 30 sec to 5 min and in all cases the superconducting phase was identified by powder X-ray diffraction and energy dispersive X-ray analysis.

A typical experimental procedure is outlined below:

5g copper 2-ethylhexanoate, 3.29g barium 2-ethylhexanoate, 3.14g calcium 2-ethylhexanoate and 8.462g thallium 2-ethylhexanoate in a minimum volume of chloroform were mixed by shaking for several hours. This precursor solution was spun onto a 1x1cm single crystal yttria-stabilized zirconia (>100< orientation) substrate at 3000 rpm for 30 sec followed by pyrolysis at 250°C for 6 min in a Lindberg box furnace. This spin/pyrolysis procedure was repeated twice more at 250°C. The coated substrate and oxide pellets with molar ratio Tl:Ca:Ba:Cu 1:3:1:3 were loaded into the gold pouch under air. The film was sandwiched between two pellets and the film surface kept from the pellet itself using a spacer made from thermocouple wire. This whole package was heated in a Lindberg 25 mm (1") tube furnace from 25°C to

a temperature of 855°C in 10 min and held for 4 min. Cooling to room temperature took a further 5 min and was achieved by opening the furnace.

Advantages of the laser ablation method include the cleanliness inherent in vacuum deposition, precise and repeatable control of the rate of film growth, control of film stoichiometry via the target composition, control of oxygen activity via the choice of oxygen species and/or plasma activation, and the ability to grow on a substrate at elevated temperature to encourage epitaxial growth.

The subject articles comprising superconductive thallium-based layers on crystalline substrates provide for an extraordinary advance over previously prepared materials. The subject articles have superconductive properties at liquid nitrogen or higher temperatures, are highly oriented and are grown epitaxially on a crystalline substrate and as shown, provide for a number of highly desirable physical and electrical properties.

With the methods described for producing the subject compositions, growth can be carefully controlled, so as to provide for highly oriented and epitaxial films. In addition, the thickness can be controlled, so as to provide for greater homogeneity and uniformity of the sol-gel film. Also, the rate of growth of the crystallites is controlled under controlled temperature conditions, to provide for substantial homogeneity.

Advantages of the sol-gel technique include the capability to coat large areas uniformly, atomic-scale mixing of the components at room temperature, low temperature synthesis of mixed metal oxides, amenability to powder, bulk, film or fiber development, as well as attaining of high chemical purities.

The laser ablation system has the advantages of safety, the system is opened at room temperature, the opportunity to prepare the superconducting Tl films in situ, and the ablation and condensation zone may be surrounded by disposable shields, where stray thallium will deposit, rate of growth and thickness can be carefully controlled, and epitaxial growth can be encouraged.

The methods described for producing films of varying thicknesses having superconductive properties are convenient, allow for coating of a variety of substrates, and can provide different physical characteristics of the superconductive film.

Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the scope of the appended claims.

Claims

1. A superconducting article comprising an oriented, epitaxial superconducting layer of thallium, optionally calcium, barium, and copper oxide on a crystal-

line substrate, said layer being at least $30 \cdot 10^{-10}$ m thick, and having a c-axis oriented normal to the crystalline substrate surface and being epitaxial to the substrate.

2. A superconducting article according to Claim 1, wherein said superconducting layer has the 2122 composition.

3. A superconducting article according to Claim 1, wherein said superconducting layer has the 2223 composition.

4. A superconducting article according to Claim 1, wherein said substrate is magnesium oxide or yttria stabilized zirconia.

5. A superconducting article comprising a superconducting epitaxial layer of thallium, barium, calcium and copper oxide on magnesium oxide said magnesium oxide being a substrate, wherein the layer is epitaxial to the substrate.

6. A superconducting article according to Claim 5, wherein said superconducting layer is the 2122 composition.

7. A microwave or millimeter device comprising an article according to any of Claims 1, 5 and 6, wherein said superconducting layer is under 1 micrometer in thickness.

8. The superconducting article of Claim 1 wherein the layer thickness is less than or equal to 2 microns.

9. The superconducting article of Claim 1 wherein the crystalline substrate consists of a single crystal.

10. The superconducting article of Claim 1 wherein the substrate is lanthanum aluminate or sapphire.

11. The superconducting article of Claim 1 wherein the epitaxial superconducting layer measures at least 3 centimeters as the smallest dimension in the a and b axes of the layer.

12. The superconducting article of Claim 1 wherein the epitaxial superconducting layer measures at least 5 centimeters as the smallest dimension in the a and b axes of the layer.

13. The microwave or millimeter device of Claim 7 wherein the device includes a resonator.

14. The microwave or millimeter device of Claim 7 wherein the device includes a delay line.

15. The superconducting article of Claim 1 wherein the

surface resistance is less than 10^{-3} ohms at 10 GHz at about 77K.

16. The superconducting article of Claim 15 wherein the surface resistance is less than 10^{-4} ohms at 10 GHz at about 77K.

17. The superconducting article of Claim 1 wherein the epitaxial superconducting layer measures at least 0.5 centimeters as the smallest dimension in the a and b axes of the layer.

Patentansprüche

1. Supraleitender Gegenstand (Formkörper), der umfaßt eine gerichtete (orientierte) supraleitende Epitaxieschicht aus Thallium, gegebenenfalls Calcium, Barium und Kupferoxid auf einem kristallinen Substrat, wobei diese Schicht mindestens 30 x 10^{-10} m dick ist und eine c-Achse aufweist, die senkrecht zur kristallinen Substratoberfläche ausgerichtet und epitaxial zu dem Substrat ist.

2. Supraleitender Gegenstand nach Anspruch 1, worin die supraleitende Schicht die Zusammensetzung 2122 hat.

3. Supraleitender Gegenstand nach Anspruch 1, worin die supraleitende Schicht die Zusammensetzung 2223 hat.

4. Supraleitender Gegenstand nach Anspruch 1, worin das Substrat Magnesiumoxid oder Yttriumoxid ist, das mit Zirkoniumdioxid stabilisiert ist.

5. Supraleitender Gegenstand, der umfaßt eine supraleitende Epitaxieschicht aus Thallium, Barium, Calcium und Kupferoxid auf Magnesiumoxid, wobei das Magnesiumoxid das Substrat ist, wobei die Schicht epitaxial zu dem Substrat ist.

6. Supraleitender Gegenstand nach Anspruch 5, worin die supraleitende Schicht die Zusammensetzung 2122 hat.

7. Mikrowellen- oder Millimeter-Vorrichtung, die umfaßt einen Gegenstand nach einem der Ansprüche 1, 5 und 6, wobei die supraleitende Schicht eine Dicke von weniger als 1 μm hat.

8. Supraleitender Gegenstand nach Anspruch 1, worin die Schichtdicke ≤ 2 μm beträgt.

9. Supraleitender Gegenstand nach Anspruch 1, worin das kristalline Substrat aus einem Einkristall besteht.

10. Supraleitender Gegenstand nach Anspruch 1, worin das Substrat Lanthanaluminat oder Saphir ist.

11. Supraleitender Gegenstand nach Anspruch 1, worin die supraleitende Epitaxieschicht Abmessungen von mindestens 3 cm als kleinste Dimension in den a- und b-Achsen der Schicht hat.

12. Supraleitender Gegenstand nach Anspruch 1, worin die supraleitende Epitaxieschicht Abmessungen von mindestens 5 cm als kleinste Dimension in den a- und b-Achsen der Schicht hat.

13. Mikrowellen- oder Millimeter-Vorrichtung nach Anspruch 7, die einen Resonator umfaßt.

14. Mikrowellen- oder Millimeter-Vorrichtung nach Anspruch 7, die eine Verzögerungsleitung umfaßt.

15. Supraleitender Gegenstand nach Anspruch 1, worin der Oberflächenwiderstand weniger als 10^{-3} Ohm bei 10 GHz bei etwa 77°K beträgt.

16. Supraleitender Gegenstand nach Anspruch 15, worin der Oberflächenwiderstand weniger als 10^{-4} Ohm bei 10 GHz bei etwa 77°K beträgt.

17. Supraleitender Gegenstand nach Anspruch 1, worin die supraleitende Epitaxieschicht Abmessungen von mindestens 0,5 cm als kleinste Dimension in den a- und b-Achsen der Schicht hat.

Revendications

1. Article supraconducteur comprenant une couche supraconductrice épitaxiale orientée de thallium, éventuellement de calcium, de baryum et d'oxyde de cuivre sur un substrat cristallin, ladite couche ayant une épaisseur d'au moins 30.10^{-10} m, ayant un axe c orienté normalement à la surface de substrat cristallin et étant épitaxiale par rapport au substrat.

2. Article supraconducteur selon la revendication 1, dans lequel ladite couche supraconductrice est de composition 2122.

3. Article supraconducteur selon la revendication 1, dans lequel ladite couche supraconductrice est de composition 2223.

4. Article supraconducteur selon la revendication 1, dans lequel ledit substrat est en oxyde de magnésium ou en zircone stabilisée à l'yttrium.

5. Article supraconducteur comprenant une couche épitaxiale supraconductrice de thallium, de baryum, de calcium et d'oxyde de cuivre sur de l'oxyde de magnésium, ledit oxyde de magnésium étant un substrat, dans lequel la couche est épitaxiale par rapport au substrat.

6. Article supraconducteur selon la revendication 5, dans lequel ladite couche supraconductrice est de composition 2122.

7. Dispositif à micro-ondes ou à ondes millimétriques, comprenant un article conforme à l'une quelconque des revendications 1, 5 et 6, dans lequel ladite couche supraconductrice a une épaisseur inférieure à 1 micromètre.

8. Article supraconducteur selon la revendication 1, dans lequel l'épaisseur de la couche est inférieure ou égale à 2 micromètres.

9. Article supraconducteur selon la revendication 1, dans lequel le substrat cristallin est constitué d'un monocristal.

10. Article supraconducteur selon la revendication 1, dans lequel le substrat est un aluminate de lanthane ou un saphir.

11. Article supraconducteur selon la revendication 1, dans lequel la dimension la plus petite de la couche supraconductrice épitaxiale, sur les axes a et b de la couche, est d'au moins 3 centimètres.

12. Article supraconducteur selon la revendication 1, dans lequel la dimension la plus petite de la couche supraconductrice épitaxiale, sur les axes a et b de la couche, est d'au moins 5 centimètres.
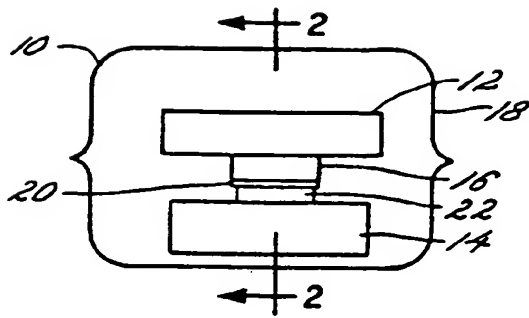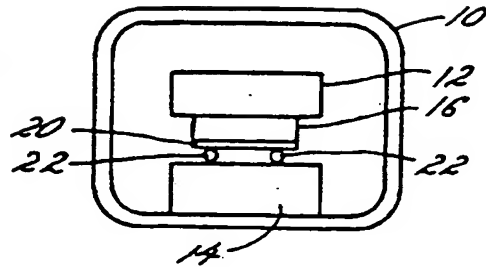
13. Dispositif à micro-ondes ou à ondes millimétriques selon la revendication 7, dans lequel le dispositif comprend un résonateur.

14. Dispositif à micro-ondes ou à ondes millimétriques selon la revendication 7, dans lequel le dispositif comprend une ligne à retard.

15. Article supraconducteur selon la revendication 1, dans lequel la résistance superficielle est inférieure à 10^{-3} ohm à 10 GHz à environ 77 K.

16. Article supraconducteur selon la revendication 17, dans lequel la résistance superficielle est inférieure à 10^{-4} ohm à 10 GHz à environ 77 K.

17. Article supraconducteur selon la revendication 1, dans lequel la dimension la plus petite de la couche supraconductrice épitaxiale, sur les axes a et b de la couche, est d'au moins 0,5 centimètre.
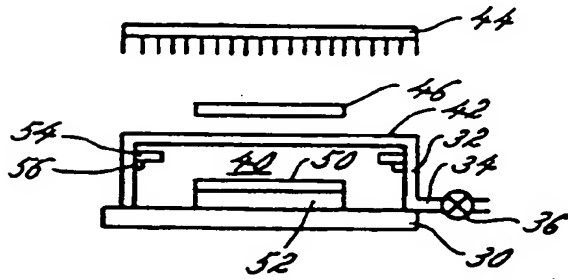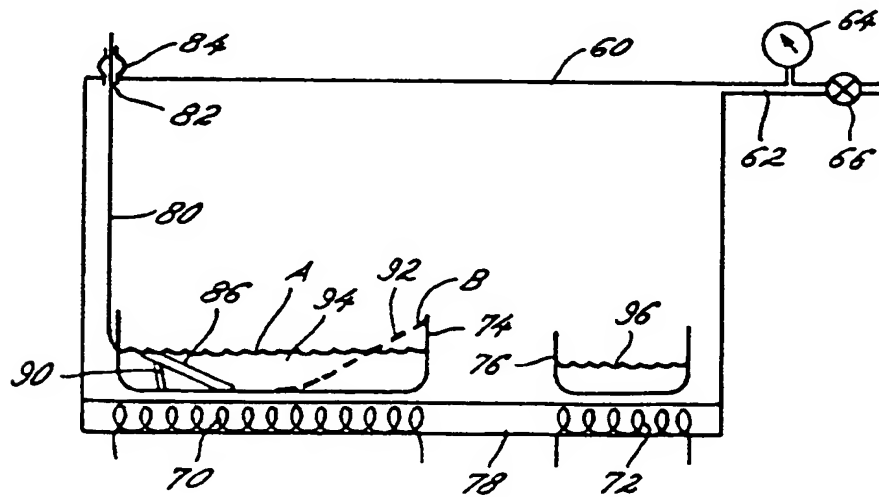
FIG. 1

FIG. 2

FIG. 3

FIG. 4

ANTENNA

MICROWAVE RECIEVER

100

102

MIXER

112

MICROWAVE FILTER

104

DISPERSIVE DELAY LINE

106

114

110

SWEPT LOCAL OSCILLATOR

OUTPUTS AMPLI-
TUDE VERSUS
FREQUENCY VERSUS
TIME SIGNAL SPEC-
TRUM AT NYQUIST
DATA RATE.

W

W

118

S

116

α   α   α   α

SMA COAXIAL CONNECTORS

FIG. 5

ANTENNA

DIGITAL INSTANTANEOUS FREQUENCY
MEASUREMENT (DIFM)

120   122

POWER SPLITTER

130

PHASE DETECTOR

136   HI

140   VII

124   132 T
DELAY LINE

134   136

V_{IOC}

DELAY LINE

134

FIG. 6